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OF EXISTING  
AND DEVELOPMENT OF NEW  
ANALYTICAL PROCEDURES  
FOR USE IN THE ANALYSIS OF  
POLYMERIC MATERIAL

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EVALUATION OF EXISTING AND DEVELOPMENT OF NEW ANALYTICAL PROCEDURES  
FOR USE IN THE ANALYSIS OF FINISHES FOR GLASS FABRIC MATERIAL

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Union Carbide Corporation

April 1960

Materials Central  
Contract No. AF33(616)-6289  
Project No. 7360

Wright Air Development Division  
Air Research and Development Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio

## FOREWORD

This report was prepared by the Union Carbide Silicones Division. Work here reported was sponsored by the Materials Laboratory under USAF Contract No. AF33(616)-6289. This contract was initiated under Project No. 7360 "The Chemistry and Physics of Materials," Task No. 73615 "Compositional Atomic and Molecular Analysis." It was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. W. R. Powell acting as project engineer. This report covers work conducted from May 10, 1959, to April 11, 1960.

All the analytical and microscopic tests and procedures reported herein were worked out by Mr. Howard Bradley and his assistants, Barbara Bierl, R. J. Lewandowski, H. F. Hillery and G. W. Heylman, of the Tonawanda Laboratory Analytical Department. The colorimetric standards are simulated rather than true colors because of fading and should be freshly prepared by the analyst. The simulated standards are enclosed in a pocket of the rear cover. The processes for glass finishing and preparation and evaluation of reinforced plastic structures were done by J. Sidlovsky, J. G. Marsden and L. P. Ziemianski. Dr. M. H. Jellinek contributed much valuable information and advice. The several phases of the program were planned and coordinated by Mr. S. Sterman.

## ABSTRACT

Essentially all of the objectives of WADD AF33(616)-6289 contract "for evaluation of existing procedures and development of new analytical methods for identifying the chemical type and amount of finish present on glass cloth" are believed to have been attained.

The strong and weak points of present methods as well as their correlation with performance are shown for vinylsilane finishes (A-172 and Garan), gamma-aminopropyltriethoxysilane finish (A-1100) and methacrylate-chromium finish (Volan A). The uniformity of loading of finish on commercially treated glass cloth has been shown. The strength of bonding has been shown by extractive procedures and by performance data.

A new simple, qualitative, rapid, colorimetric series of tests has been developed for identifying the above finishes. New, improved quantitative procedures have also been developed for each finish.

An electron microscopy replica technique has been developed which for the first time allows the actual surface and configuration of the finishes on glass to be seen, giving a new tool and new insights into the way finishes behave on glass.

## PUBLICATION REVIEW

This report has been reviewed and approved.

FOR THE COMMANDER:

F. F. BENTLEY  
Chief, Analytical Branch  
Physics Laboratory  
Materials Central

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## SUMMARY:

This is the final report on WADD-AF33(616)-6289 contract, "for evaluation of existing procedures and development of new analytical methods for identifying the chemical type and amount of finish present on glass cloth."

We believe that we have achieved all the objectives set forth in the contract. In particular, we can now determine the type, quantity and quality of finish on any given piece of glass cloth. These results are summarized in detail below:

1. We have shown in detail the advantages, disadvantages, correlation with performance of the present analytical methods for vinylsilane finishes (A-172 and Garan); gamma-aminopropyltriethoxysilane finish (A-1100) and methacrylate-chromium finish (Volan A).
2. We have shown how the existing methods may be used to show uniformity of finish loading on glass cloth by selection of definite sites on a roll of glass cloth for analysis. We have shown that commercially-finished cloth is of adequate uniformity for the rolls sampled so that loading should not be a factor in variation of performance.
3. We have shown the strength of bonding of each finish to glass by both correlation between loading and performance and by extractive procedures for ease of removal. A-172 is very strongly bonded; A-1100 and Volan much less so. All three show strongest bonding in the layers closest to the glass.
4. We have developed a completely new, integrated, qualitative, colorimetric series of procedures for identifying the above finishes quickly and simply. Five dyes or colorants are used and, with a little practice, only 25 minutes are needed to identify all finishes.
5. We have developed new procedures for quantitative determination of these finishes. These include:
  - a. a new carbon procedure for A-172 or A-1100,
  - b. a new specific "vinyl" procedure for A-172,
  - c. a new colorimetric test for A-172 (Rhodamine B),
  - d. a new colorimetric test for A-1100 (sodium nitroprusside),
  - e. new methods for the chromium in Volan A ( $\text{Na}_2\text{CO}_3$  fusion and perchloric acid digestion).
6. We have developed an electron microscopy replica technique which for the first time allows the actual surface and configuration of the

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Manuscript released by the author 24 June 1960 for publication as a WADD Technical Report.

finishes on glass to be seen, giving a new tool and new insights into the way finishes behave on glass. Loadings which correlate with chemical analyses can even be calculated from the electron micrographs. In general, finishes do not deposit as a continuous layer but rather in discrete polymer units. This effect, along with a "channeling" effect, probably explains why a loading calculated to give a monofilm is never sufficient for optimum properties.

#### DISCUSSION:

This entire report deals with analyses, evaluation and handling problems on high quality, heat cleaned glass cloth. In this case, 181-112 was used throughout. The results should apply to any other similar heat cleaned glass cloth; but, because of differences in handling, fiber diameter and length and techniques of "finishing" or "sizing," it should not be assumed that the same results would necessarily be obtained with woven roving, mat or with woven cloth of widely-different specification.

The 181 glass cloth is woven from strands composed of approximately 600 glass filaments, 5-8 microns in diameter; the appearance of a section of a glass strand is shown in Appendix XIX.

The A-172 and A-1100 finishes are applied by dipping the glass cloths in an aqueous solution of the finish; the loading is controlled by the concentration of the dipping solutions and the rate of withdrawal of the cloth. The treated cloth is then passed through a drying oven and the water is completely evaporated. During the drying process, the alkoxy groups of the A-172 and A-1100 are replaced by hydroxyl groups which condense and leave resins having the general formula  $[\text{RSiO}_3/2]$ . The Volan A finish is applied in a manner similar to A-172 and A-1100 finishes except that a washing and subsequent drying step is required to remove water-soluble salts formed during the neutralization part of the process. According to DuPont literature, the Volan A finish is a polymer having the empirical formula,  $\text{C}_4\text{H}_6\text{O}_5\text{Cr}_2$ .

In analyzing glass cloths finished with A-172 or A-1100, it is a well-established custom to report the analyses in terms of weight per cent A-172 and A-1100, even though the finish on the cloth, after curing, no longer has the chemical composition of the parent A-172 or A-1100. For example,

the A-172 in the finishing solution has the formula  $H_2C=CHSi(OC_2H_4OCH_3)_3$  and after hydrolysis and curing it assumes the formula  $[H_2C=CHSiO_3/2]$  which is the same as the Garan finish at this point.

# I. Existing Methods of Analysis:

## A. A-172 and Garan:

A-172 or Garan finish loadings on glass fabric are determined by means of a carbon analysis, and then relating the carbon content to the finish loading. The analytical procedure used to determine carbon content is in Appendix XIII. but has now been supplanted by Appendix XII. As heat cleaned glass cloth prior to finishing contains small amounts of carbon, this is taken into consideration when the finish loading is calculated. A sample calculation of Garan or A-172 finish loadings is as follows:

Carbon content of A-172-finished fabric	$0.075 \pm 0.006$
Carbon content of heat cleaned fabric	<u><math>0.015 \pm 0.006</math></u>

Corrected carbon content	$0.060 \pm 0.006$
--------------------------	-------------------

Weight per cent A-172 on glass fabric =

$$\frac{\% C \times H_2C=CHSi(OCH_2CH_2OCH_3)_3}{2 C}$$

or

$$0.060 \times \frac{280}{24} = 0.70 \pm 0.07$$

If the finish is Garan, the conversion factor is 190/24 instead of 280/24.

A new carbon method which is much faster than the conventional combustion train is now being used. This is the "Leco Carbon Determinator," manufactured by Laboratory Equipment Corporation, St. Joseph, Michigan, at a price of \$3700. This unit cuts time per analysis from about one hour to six minutes and appears to be more sensitive and precise. Based on both laboratory and commercial practice, these carbon analyses appear to correlate with estimated loading based on solution concentration of the finish and per cent wet pickup of the cloth, as well as with performance (wet and dry flexural strength) of polyester laminates.

In commercial practice, an optimum loading of 0.5% as A-172, based on cloth weight is designated to allow for production variation on either side, since a plateau of performance exists from about 0.3% to 0.8%. A detailed table of these loadings, analyses and performance is shown in Appendix I and II.

These analyses show average values; individual determinations based on where the sample was cut from the swatch show analytically significant deviations. Fortunately, even these deviations are not significant in

terms of performance because of the broad plateau of good performance. Furthermore, these deviations are believed to be due to the way a small swatch is handled and dried in the lab and are not true for commercial production where continuous and uniform wet pickup and drying takes place.

#### B. A-1100:

The A-1100 loading on glass fabric is determined by means of a nitrogen determination and then relating the nitrogen content to A-1100. The analytical procedure used to determine nitrogen content is attached. As heat-cleaned glass cloth prior to finishing shows a small blank, this cloth must be analyzed for nitrogen content and a suitable adjustment be made in calculating the A-1100 loading. A sample calculation is presented below:

Nitrogen content, A-1100-finished cloth	0.022%
Apparent Nitrogen content, heat-cleaned cloth	<u>0.001%</u>
Corrected nitrogen content	0.021%

Corrected weight per cent A-1100 on glass cloth =

$$0.021 \times \frac{221}{14} = 0.33\%$$

As in the case of A-172 above, good general correlation exists between loading determined by wet pickup, analyses for nitrogen and performance. These data are presented in detail in Appendix III and IV. For room-temperature laminates, it appears that loadings as low as 0.1% A-1100 are in the useful range. For high-temperature laminates, this minimum useful value seems to be about 0.4% A-1100. For commercial use, a safety factor seems desirable and higher loadings should be recommended, especially since the curve of performance versus loading is quite flat above these minimum values, up to at least 1.5% A-1100 loading on cloth.

The correlation of loading by wet pickup and both carbon and nitrogen determinations is quite good but with a trend in the higher loadings for the actual loading to be somewhat less than that estimated by wet pickup. This may be due to laboratory handling and draining of small swatches. Because the performance data, as shown in Appendix IV are so flat, the minor deviations in carbon and nitrogen values seem insignificant.

#### C. Volan A:

The Volan A loading on fabric is determined by analyzing the finished cloth for chromium content and then relating this to the Volan A polymer. The test for chromium content is based on oxidation of chromium to chromate by sodium hypobromite treatment and subsequent colorimetric determination using diphenylcarbohydrazide reagent. The time required for this method is approximately 45 minutes. We have not studied this method.

## II. Uniformity of Loading:

The uniformity of loading of commercially- and laboratory-treated cloth was determined by analysis of geometrically spaced bits from a large swatch of cloth for each finish, using standard methods for carbon, nitrogen or chromium.

The results show that commercially-treated cloth is much more uniform than laboratory-treated small swatches, because of exaggerated drainage and migration problems in laboratory treatment. Typical analysis of commercial cloth for A-172, A-1100 and Volan are shown in Appendix V, VI and VII. The variations are small enough that no performance differences could be expected, based on Appendix II and IV. Similar data for laboratory swatches were obtained but are not shown. Even with these, where the variation is much greater, it still is not enough to affect performance in the recommended concentration range.

In Appendix VII, note that the Volan loading determined by carbon is very low compared to that measured by chromium and the postulated ratio of 4C per 2 Cr, but uniformity for either carbon or chromium is good.

## III. Degree of Bonding:

Since the purpose of these finishes is to act as coupling agents through which large organic molecules may be linked to the substrate, studies were made to determine the degree of bonding of A-1100, A-172 and Volan A to the glass substrate. Degree of bonding may refer to (a) the finish which is bonded directly to the glass substrate or (b) the finish which is attached to underlying finish.

We used Soxhlet extraction tests for protracted periods of time and made extensive studies with electron and phase microscopes of the specimens being studied. The solutions which were used in the extraction tests were analyzed chemically and by infrared spectrometry.

### A. A-172:

Performance versus loading data in Appendix II implies that the strength of bonding of A-172 (to underlying layers) begins to fall off as the total loading increases beyond about 0.75%.

Extraction data with several solvents and loadings confirm this. For example, four-hour Soxhlet extractions with carbon tetrachloride and acetone on cloth of several loadings were run. 181 cloth with 0.25% and 0.67% A-172 loadings showed no extraction at all, as determined by infrared analysis; however, 181 cloth with 2.0% A-172 loading showed about 20% extraction by acetone. Styrene could not be used in the Soxhlet method since it polymerized, but cold extraction of the lower loadings again showed no A-172 removed.

A four-day extraction with water reduced the loading of one sample only from 1.1% A-172 to 0.6% A-172.

It is apparent that A-172 forms a firm bond to glass and that for loading in the recommended range, vinylsiloxane also bonds strongly to itself.

#### B. A-1100:

The degree of bonding of A-1100-loaded cloth has been studied by extraction with distilled water in a Soxhlet and analyzing for A-1100 content before and after. These data are summarized in Appendix VIII. It is apparent that hot water (four hours Soxhlet) removed 75-94% of the A-1100, but it seems clear that a small, well-bonded layer also exists which is not removed from the glass even after four hours. This water sensitivity does not occur, of course, after a laminate is prepared because of reaction with the resin and the known improved resistance of the structure to water. It would be of interest to prepare a laminate from water-washed A-1100-finished cloth to see if the very low residual loading would perform better than an equivalent loading applied in the normal way. This might throw light on the uniformity of present techniques of finishing.

In a separate, shorter test in boiling water, five-minute exposure of A-1100-finished cloth removed an appreciable amount of A-1100 from laboratory-prepared samples of finished cloth; even fifteen-minute boiling failed to remove any A-1100 from commercially-treated cloth. This suggests that commercial cloth is more tightly bonded than laboratory cloth, possibly because of more thorough cure.

Another specimen of A-1100-finished cloth was given four hour Soxhlet extraction with benzene. The loss of A-1100 as indicated by analyses was only 19% and the C/N ratio of the residual finish conforms to  $\text{NH}_2(\text{CH}_2)_3\text{SiO}_3/2$ .

These data show that there is a very tightly-bonded layer of gamma-aminopropylpolysiloxane close to the glass but that excess polymer is much more weakly bonded.

#### C. Volan A:

Typical Volan-finished cloths are listed in Appendix IX; an electron micrograph of one of these is shown in Figure 9.

The electron micrograph indicates that the Volan A is uniformly distributed in aggregates, or particles (or perhaps polymeric units), whose diameters vary between 100 and 300 angstroms. Consideration of these dimensions and the amount of finish present (0.13% Volan A calculated as the polymer  $\text{C}_4\text{H}_9\text{O}_5\text{Cr}_2$  on the basis of Cr; 0.04% Volan A on basis of C) suggests that, in this case, we are not dealing with a multi-layered finish; therefore, any degree of bonding information obtained on tests with this specimen should, for the most part, indicate the strength of the Volan A-to-glass bond. Four hour Soxhlet extractions of this material with water and with isopropanol failed to remove any appreciable amount of finish.

In order to learn how strongly Volan A is bonded to underlying Volan A, we tried to prepare more heavily loaded cloths. Appendix X shows that we were unsuccessful in preparing a heavily loaded cloth, except in two cases (first and third) where we purposely omitted the water wash recommended by DuPont. In those two cases, it is interesting to note that the carbon-chromium ratio is stoichiometrically rational for Volan A. In preparations 2 and 4 the recommended water wash was included and the loadings retained by the cloths were only 0.17% and 0.21% on the basis of chromium compared with 0.08% and 0.14% on the basis of carbon.

Notice that in all cases (preparations 1-4, Appendix X), the loadings "after Soxhlet-water extraction" were essentially the same. Also, preparations 2 and 4, which were given the recommended one minute water wash, were not altered very significantly by an additional four day Soxhlet extraction.

These data and the electron micrograph studies indicate that Volan will readily form a light (up to 0.2% loading), well-bonded layer of Volan A-to-glass, and that bonds between Volan A and Volan A are quite weak.

#### IV. New Qualitative Methods of Analysis:

Simple, rapid means for identifying the type of finish on glass cloth have been needed for a long time to aid fabricators in checking their inventory or operating procedure where specifications are rigid. Qualitative tests existing when this work was started include (a) a specific test for A-1100 finish using sodium nitroprusside to react with the A-1100 amino group, developing a violet stain on the cloth (Union Carbide Corporation - Silicones Division - 7160-27 unpublished notes), (b) a specific test requiring about one-half hour for Volan A, based on a color reaction between sodium peroxide-extractable-chromium and diphenyl carbazide (Boeing Airplane Company D3-219), and (c) Boeing's (D3-219) rhodamine B dye test (requiring 25 minutes) for A-172 and Volan, in which the A-172-dyed cloth assumes a violet hue, while the Volan A acquires a faint pinkish color; however, to the best of our knowledge, these tests had not been integrated to a scheme useful to fabricators.

We have explored the aforementioned tests. Test (a) is rapid and reliable. Test (b) requires a filtration and consumes more time (30 minutes) than is necessary; we have simplified this so that the test can be made in 10 minutes by using a perchloric acid leach, diluting with water and adding the diphenyl carbazide directly to the solution in the test tube. Test (c) was not able to differentiate A-172 and Volan for us; nevertheless, it is useful for a confirmatory test. On the other hand, we considered 25 minutes as much too long for a qualitative test; therefore, we modified this test so that it required only 10 minutes.

We have developed a much improved qualitative analysis scheme which permits rapid identification of A-172, A-1100 and Volan-finished and of unfinished glass cloths by an operator who is not a highly-skilled chemist.

All the tests outlined in Appendix XI are applied directly to the cloth and can be performed rapidly by a nonskilled operator; the approximate time necessary for each ranges from 1 to 10 minutes depending on the test (See Table 2). Very specific tests have been established for A-1100 and for Volan-finished cloths; however, for A-172-finished and for "blank" cloths, the tests are somewhat less specific and confirmatory tests are recommended for positive identification.

Since A-1100 finish can be identified immediately and specifically with bromcresol green or sodium nitroprusside and since failure to eliminate it from consideration might introduce ambiguities into subsequent tests, a test for this finish should be carried out first. Both bromcresol green and sodium nitroprusside impart a color to the A-1100-finished cloth by reacting with the amino group. The bromcresol green test is more rapid and is somewhat more sensitive than the sodium nitroprusside test and should, therefore, be used as the primary test with the nitroprusside as a confirmatory test, although in our experience no confirmatory test has been required for A-1100.

The second and third tests to be performed (see Table 1) on the remaining unidentified cloths are the Methylene Blue Wick Test and the Methylene Blue Color Test. The "wick" test is based on the fact that A-172-finished cloth is water repellent and, therefore, does not "wick" up an aqueous dye solution, while the other types of cloth readily "wick" up the dye. The "color" test differentiates A-172, Volan and blank cloths since these cloths each show a different shade of blue when dyed with the methylene blue. Since neither of these tests has a known, sound chemical basis, erroneous results may occur from time to time due to such things as poorly applied finish, contamination, etc. Therefore, it is recommended that a confirmatory test for the type of finish indicated should be made.

The Diphenyl Carbazide Test is a specific chemical test for Volan A finish; chromium from the Volan A coating is leached and oxidized with fuming perchloric acid and is then diluted with water and reacted with diphenyl carbazide to form a red-colored complex. Where facilities for handling perchloric acid are available, this is the test which should be performed for positive identification of Volan-finished cloth.

The Rhodamine B Test, unlike the Diphenyl Carbazide Test, is not a chemical test. It is instead a dye test which can be used to identify A-172, blank or Volan cloth. This test covers two procedures; the first of these, a modification of the Boeing Airplane Company's test (Boeing reprint D3-2159), distinguishes blank cloth from Volan or A-172-finished cloth and the second procedure differentiates A-172 cloth from Volan A and blank cloth. Identification of Volan A cloth, therefore, requires using both dyeing procedures since it will dye with the first but not with the second. It is good practice to carry along a piece of cloth known to be unfinished through the procedure as a control, since differences in technique of individuals could somewhat influence results. When handling dyes, such as rhodamine B, rubber gloves should be worn to protect the hands of the operator from stains, and tweezers should be used to hold the pieces of cloth being tested in order to avoid excessive handling.



Any of the four cloths (Volan, A-172, A-1100 and blank) can be positively identified in about 15 minutes and all four can be distinguished and identified with assurance in a total of about 25 minutes. The entire scheme is described in working detail in Appendix XI.

## V. New Quantitative Methods of Analysis:

### A. A-172:

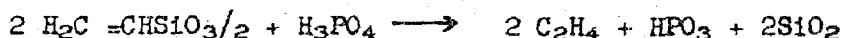
#### 1. Leco Carbon Apparatus:

The only method previously used to determine A-172 loadings was the total carbon determination using a conventional carbon-hydrogen train with platinum catalyst. This method is quite reliable, provided the blank carbon is known. The conventional carbon-hydrogen train has been abandoned in favor of the "Leco" apparatus for total carbon. This apparatus is far quicker and simpler to operate than the classical C-H train and is described in Appendix XII.

It would seem quite logical to develop a method utilizing the double bond in the A-172 molecule, calculating the amount of loading on the basis of bromine absorption; however, our experience has been that bromine does not readily add to vinyl groups attached to silicon and in this case we were dealing with vinyl compounds which could not be dissolved from the glass and which in many cases were protected from the bromine by overlying A-172 finish.

#### 2. Ethylene Evolution Method:

About 1950 (unpublished work of this laboratory), it was found that strong acids such as sulfuric acid could cleave certain groups from silicon. In the present study we applied this principle using phosphoric acid to the determination of vinyl content of A-172-finished glass cloth. The postulated reaction is:



The validity of the assumption has been verified by mass spectrographic and gas chromatographic analyses of vinylsiloxane resin prepared by hydrolyzing and dehydrating A-172 and by comparing analyses based on carbon with those based on evolved ethylene (see Appendix XIV, Table 1). To utilize the reaction, the evolved ethylene is trapped on cold silica gel and subsequently determined by gas chromatography.

The obvious virtue of this ethylene evolution method is that it is specific in the area being considered (A-172, A-1100 and Volan). It is furthermore the most sensitive and accurate means of detecting vinyl-Si groups easily surpassing the best colorimetric tests devised. It does not, however, employ simple laboratory apparatus and it requires about one hour to complete a determination. This should be considered as an umpire method and should find application where more exact information is required, particularly in research studies.

The detailed procedure is described in Appendix XIV.

### 3. A-172 Control Test Using Rhodamine B;

To meet the demand for a rapid, simple control test, we tried a number of dyes after having first shown that it was not feasible to extract the finish from the cloth for this purpose. Böing (reprint D3-2159) showed that A-172- or Garan-finished cloth could be dyed with rhodamine B, but that Volan A also dyes. We have modified this procedure so that Volan A no longer retains the dye. This modification has been described in Appendix XI, Qualitative Procedure. To apply this in a quantitative way, we found it necessary (as with A-1100-nitroprusside, below) to grind the finished cloths before applying the dye to expose all the layers of vinylsiloxane. The procedure is detailed in Appendix XV.

### B. A-1100:

Existing methods for quantitatively determining A-1100 loadings are based on total nitrogen or total carbon determinations. A method for determining total nitrogen by sodium hydroxide fusion of the "finished" cloth and titration of the evolved ammonia is described in Union Carbide Corporation Silicones Division circular SF-1096B and in a publication by Bradley and Neal [Anal. Chem. 31, 1925 (1959)]. This method is specific, sensitive and precise; nothing more reliable has been found.

The total carbon determination had always been done by the classic semimicro carbon-hydrogen train, using a platinum catalyst and an auxiliary trap to remove objectionable oxides of nitrogen; however, we have found that the new Leco Carbon Determinator can turn out carbon results extremely rapidly and with satisfactory precision, but interpreting the carbon values is sometimes difficult because of variation of carbon in the blank cloth from batch to batch. No such uncertainty exists with the nitrogen method. If a reliable sample of blank cloth is available, Leco equipment and method stand out. It requires only six minutes to determine the A-1100 loading by the Leco method and one hour by the more specific nitrogen fusion. Appendix III offers a comparison of the nitrogen-fusion and Leco carbon methods. The Leco method is described in Appendix XII; reference to the nitrogen-fusion method has been given.

A rapid colorimetric control test using sodium nitroprusside for estimating the A-1100 loading within 0.1% has been developed. It is necessary to grind the sample before making the test in order to liberate the amino groups for the nitroprusside reagent. Probably the reason for this is that much of the amino-alkylsiloxane is present in a multi-layered coating and the nitroprusside either cannot find the amines or, if it does find them, the eye cannot perceive the color at those points. The nitroprusside amino color is not stable for any appreciable length of time, therefore, it is necessary to compare the colors as soon as they are developed. Details are discussed in Appendix XVI.

We have also been able to compare the colors produced by A-1100-finished cloths when treated with bromocresol green solution. A quantitative procedure could be but has not yet been established on this basis. The colors produced with bromocresol green are more stable than those produced with nitroprusside, but the latter are more readily differentiable.

### C. Volan A:

DuPont recommends using a total chromium determination to indicate the Volan A loading. This seems logical since chromium should be a reliable parameter and its determination can be effected expeditiously. We have developed a method for the quantitative determination of chromium in Volan-finished cloth, using a sodium carbonate fusion to "open up" the sample, following with oxidation of any unoxidized chromium with permanganate and subsequent titration with ferrous sulfate. Time required is 35 minutes.

Serious consideration was given to determining Volan A on the basis of a carbon determination, since only six minutes is required for this determination by the Leco method. Unfortunately, the loadings as indicated by the carbons were significantly lower than those based on total chromiums. To make sure that we were not missing any of the carbon, we ran several check analyses using red lead flux to ensure absolute decomposition of all carbonaceous material. These check analyses were run with hot catalyst following the combustion zone to make sure that no readily volatile carbon was avoiding oxidation. The results showed excellent precision.

Appendix IX offers a comparison of Volan A loadings based on carbon and on chromium determinations.

We wished to develop a rapid quantitative control method for Volan A, similar to those developed for A-1100 and A-172. Since it was established that rhodamine B would dye Volan-finished cloths, we explored the quantitative aspects of this test.

The Volan cloths available to us at the time were those listed in Appendix IX. Note that the maximum spread in loadings is only 0.08%. When we applied rhodamine B to these specimens using our grinding technique, they were indistinguishable. The specimens had acquired a good color but it was apparent that we could not detect differences of loading of less than 0.1%.

We then tried to prepare more heavily loaded Volan cloths (Appendix X) using the DuPont procedure but we were unable to produce finished cloths carrying more than 0.2% Volan A expressed as the polymer,  $C_4H_8O_5Cr_2$ .

We, therefore, abandoned efforts to develop a quick color test for Volan A loading.

Appendix XVIII includes two methods for determining Volan A loading on the basis of chromium content; one is the  $Na_2CO_3$  fusion method, mentioned above, the other is a perchloric acid digestion method.

### VI. Electron and Optical Microscopy:

In order to obtain a better understanding of the nature of these finishes on glass cloths, electron and light microscope studies of the bland and finished cloths were made.

Light microscope examination showed that a typical strand in a glass cloth is composed of a bundle of cylindrical filaments whose diameters

vary between 5 and 8 microns. These rods are not tightly packed, so that liquids and gases can penetrate to the inner rods with varying degrees of ease. The exterior of each strand is shown to have a corrugated appearance (see Appendix XIX). When a cloth is treated with one of the finishing solutions, the solution on the glass strands tends to concentrate in the channels formed at the intersections of the filaments. The result is that, although there is probably a fairly uniform polymer finish over all the filament surfaces, a major portion of the excess loading will deposit in the inter-filament channels and appear as oversized agglomerates whose attachment to the substrate is not as secure as that of the smaller particles. This buildup has been observed with both phase and electron microscopes. See Figures 1, 3, 4, 6, 12, 13 and 14.

#### A. Electron Microscopy:

It is interesting to compare the electron micrographs of the three finishes. Remember that these are replicas, not direct photographs, and that you are looking down at a cylinder (or corrugated surface in part) which has been unfolded and laid out so that you may see the imprints left by the surface irregularities of the specimen.

Figure 1 shows heavy strips of A-1100 resin running parallel to the filament axis. These strips, located in the channels between two filaments, represent an appreciable fraction of the loading. Observe that the distance between the strips is 2.4 microns and that the distance between the outer edges of the two strips is 5.7 microns. This is rational with our description of a glass strand composed of cylindrical filaments 5 to 8 microns in diameter. Notice also the much lighter loading between these strips. This will show up better at higher magnification.

Figure 2 shows a smaller area of the same A-1100-finished cloth after it was extracted with water for four hours. The magnification in Figure 2 is 80,960X compared with the 21,440X of Figure 1.

Figure 3 shows an 80,960X magnification of a 0.1% A-1100 cloth. Note the tendency to fill in the inter-filament channels. Compare this with Figure 2 where the magnification is the same and the loading nearly identical. Observe that the field in Figure 2 is much more homogeneous. The specimen shown in Figure 2 had, previous to its water extraction, carried 1.6% A-1100 (Figure 1) and this was reduced to 0.08% by a four-hour hot water extraction. The specimen shown in Figure 3 had never been loaded beyond 0.1% and it failed to acquire the homogeneous distribution desired. This may help to explain why it is necessary to load cloths somewhat beyond the theoretical requirements in order to attain satisfactory coupling performance. This does not mean that there is no finish present in the smooth areas of the picture. On the contrary, if it were possible to have an absolutely smooth finish, it could escape detection by this technique. This will be discussed more fully later.

Figure 4 is a low magnification (9240X) picture of A-172 finish (0.47% loading). Notice how the deposit is concentrated towards the inter-filament channel.

Figure 5 is a 66,500X magnification of a 0.26% A-172 loaded cloth. The loading as calculated from the electron micrograph is 0.19%.

Figure 6 (21,440X) shows an interfilament buildup on a cloth whose average loading is 0.26% A-172. The loading in the interfilament channel, calculated from the micrograph, is 2.43%.

Figure 7 shows, at 66,500X magnification, a specimen which had a 0.03% A-172 loading based on chemical analysis. The loading calculated from the picture is 0.05%.

Figure 8 shows a heterogeneous area of an A-172-finished filament from a cloth which was shown by chemical analysis to have an 0.6% loading. The calculated loading for the field shown in this plate is also 0.6%.

Figure 9 is a typical area of a Volan-finished cloth carrying 0.13% Volan A load. We have not developed a mathematical formula for calculating the Volan A loading from the electron micrographs.

Figures 10 and 11 show surfaces of heat-cleaned filaments indicating respectively the maximum and average roughness to be expected. This should aid in interpreting the electron micrographs. Note that these magnifications are 80,960X. Micrographs at lower magnification should show little or no interference from this background. The mathematical formula developed for calculating A-172 loadings from these electron micrographs is included in Appendix XX.

Considering the nature of the deposits, particularly the A-172 and the maximum roughness of surface which may be encountered in the blank, it is impossible to interpret micrographs of finishes where the loadings are below 0.02%. This will become clearer if we consider (a) that our replica technique cannot, with certainty, resolve (or distinguish from blank roughness) particles of less than 40 angstroms diameter and (b) that a monolayer of 5 angstroms hemispheres of A-172, tightly packed, would only amount to 0.01% loading. If the finish were a continuous, smooth film 2.5 Å thick, the loading would be 0.017%. In neither case would we be able to see the deposit with the equipment and techniques we have employed.

To speculate further, if there were a continuous, smooth finish 25 Å thick, it would amount to 0.17% A-172. This might be possible for the cloths whose total loadings were much in excess of 0.4 or 0.5% but such an idea is not consistent with the data for the lower loadings, where we are able to measure and "see" as much loading as we can find by chemical analysis. For example, Figure 7 shows clearly resolved particles whose calculated concentration of 0.05% agrees with the chemically determined loading of 0.03%.

As far as coupling efficiency is concerned, it should not matter whether the finish is a continuous film or intermittent islands, just so long as the coupling sites are plentiful and never too far distant from nearest neighbors.

Figures 13 and 14 show inter-filament buildup of Volan A on Volan-finished cloth before they were washed to remove excess salts.

#### B. Optical Microscopy:

Figure 12 is a light microscope photomicrograph of 1.6% A-172 finish on glass filaments at maximum magnification (oil immersion lens) using a micrometer eyepiece, the scale of which is superimposed on the specimen. The smallest division on the micrometer scale is equal to 0.62 micron. It is apparent that on the heavily loaded cloths there is some buildup of gross spherical particles (up to 2 microns diameter) which are loosely attached. Indeed, these extra-large particles can be detached by stirring the preparation in oil. Fortunately, these extra-large particles are seldom found on cloths loaded with less than 0.6% A-172, although they have been observed on cloths of only 0.3% loading; they are found with increasing frequency on the more heavily loaded cloths. The tendency is for the grosser buildup of finish to occur in the channels of the strand.

Attempts were made to study the finishes on the glass filaments using a phase microscope and an A-O-Baker interference microscope. The phase microscope seemed to offer some advantage in observing the type of particles shown in Figure 12. The interference microscope would probably be very useful for measuring the thickness of extremely thin, transparent coatings on perfectly flat, thin, transparent specimens, since it is rated as being capable of measuring  $1/300$  of a wavelength of light. This would imply that coatings 10 Å thick might be measurable. Unfortunately, the coatings that we were investigating were on a cylindrical substrate and we were not able to detect anything with this microscope that could not be observed equally well with an ordinary light microscope.

## APPENDIX I

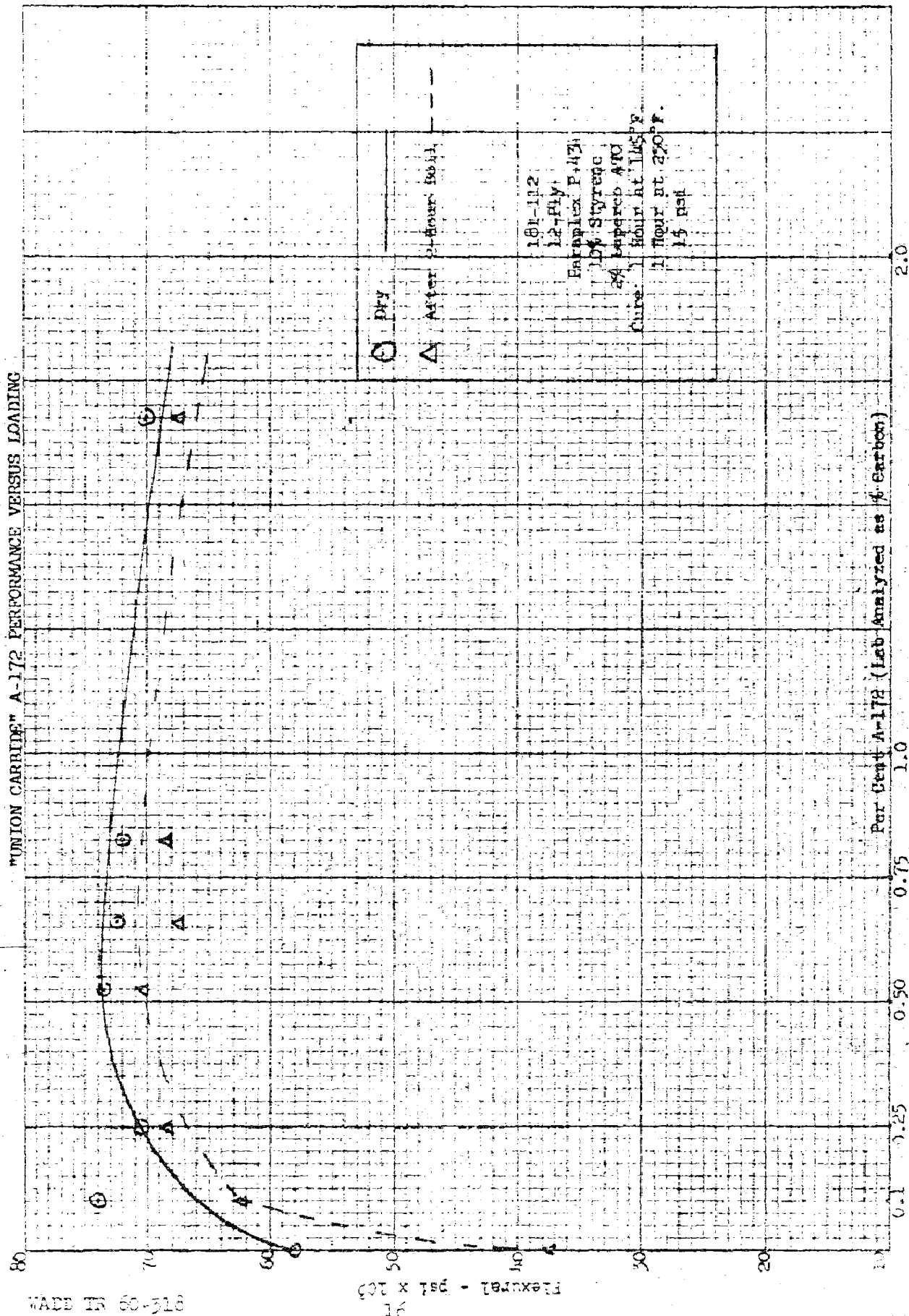
### Relationship of Flexural Strength Properties of Polyester Laminates to A-172 Loadings on the Glass Cloth Reinforcement

<u>Estimated % A-172</u>	<u>% A-172 by Carbon Analysis</u>	<u>Average Flexural Strength, psi</u>		<u>Per Cent Retention</u>	<u>% Resin Content</u>	<u>Thickness (Inches)</u>
		<u>Dry</u>	<u>2-Hr. Boil</u>			
0.0	--	58,200	37,300	64.2	34.7	0.116
0.1	0.104	74,200	62,500	84.3	34.0	0.116
0.25	0.245	70,400	69,200	98.3	34.6	0.117
0.50	0.524	73,800	70,600	95.7	34.6	0.117
0.75	0.655	72,500	67,300	92.8	34.5	0.115
1.0	0.82	72,000	69,000	95.8	35.7	0.116
2.0	1.66	70,000	68,000	97.2	33.8	0.117

#### Laminate Composition

Resin .....	Paraplex P-43 (Rohm and Haas) diluted with 10% styrene
Catalyst .....	2% Luperco ATC
Reinforcement .....	12 ply, 181 glass cloth
Curing Temperatures ...	1 hour at 145°F., 1 hour at 245°F.
Pressure .....	Pressed to 1/8" stops
Laminating Procedure ..	Standard wet layup

# APPENDIX II





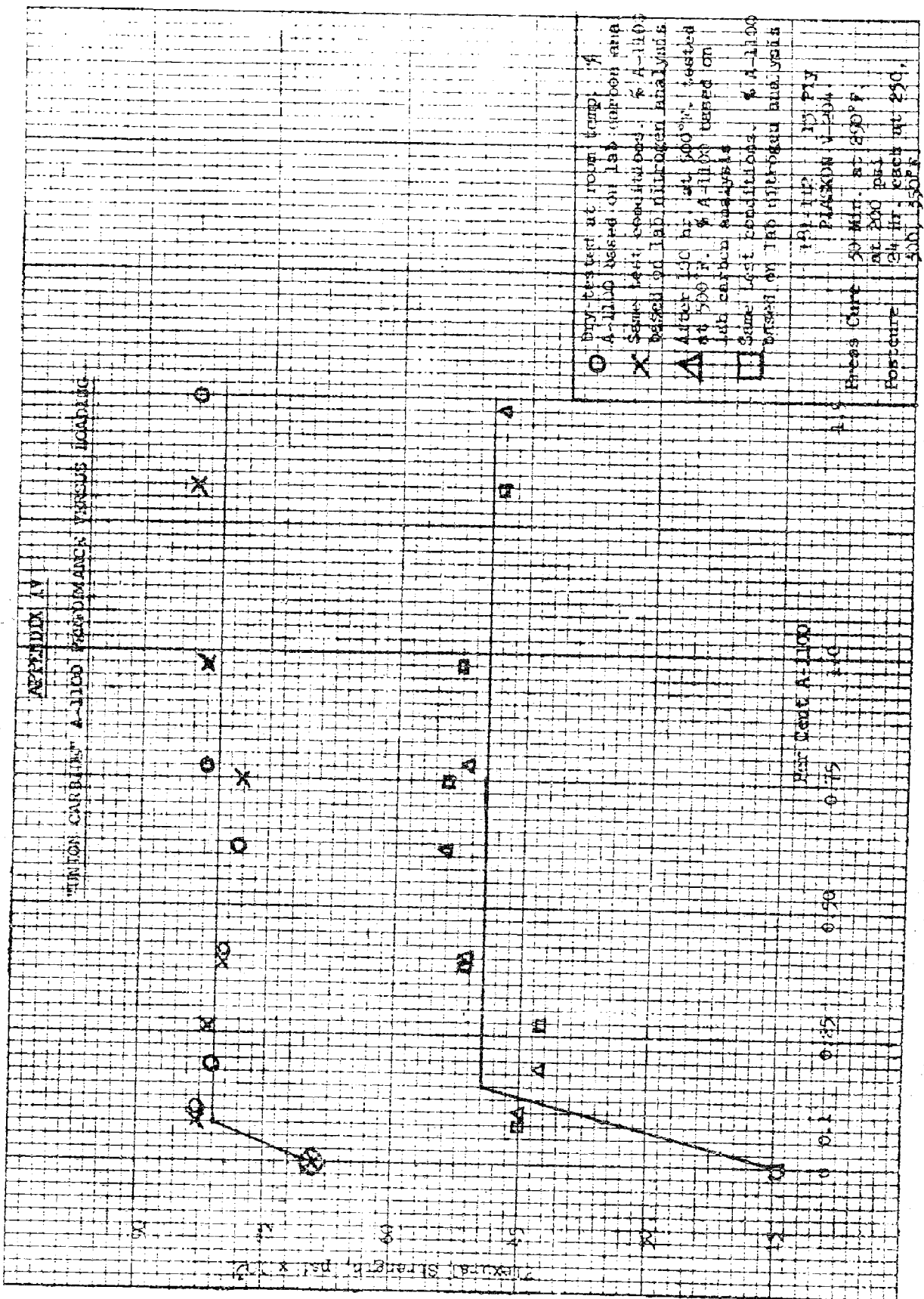
### APPENDIX III

# Relationship of Flexural Strength Properties of Phenolic Laminates to A-1100 Loadings on the Glass Cloth Reinforcement

Estimated % A-1100	Actual % A-1100		Avg. Flexural Strength, psi		Per cent Retention	% Resin Content	Thick- ness Inches
	By Carbon Analysis	By Nitrogen Analysis	Room Temp. Dry	Tested at 500°F. After 100 Hours at 500°F.			
0.0	---	---	59,500	13,200	19.0	28.2	0.112
0.1	0.10	0.08	83,300	45,900	55.2	27.0	0.104
0.25	0.19	0.27	82,200	43,200	52.6	28.1	0.109
0.50	0.41	0.39	80,600	51,900	64.0	29.2	0.114
0.75	0.73	0.76	77,900	54,500	69.0	31.9	0.118
1.0	0.92	0.96	82,500	52,300	63.4	25.2	0.110
2.0	1.4	1.6	84,300	48,500	57.6	29.4	0.111

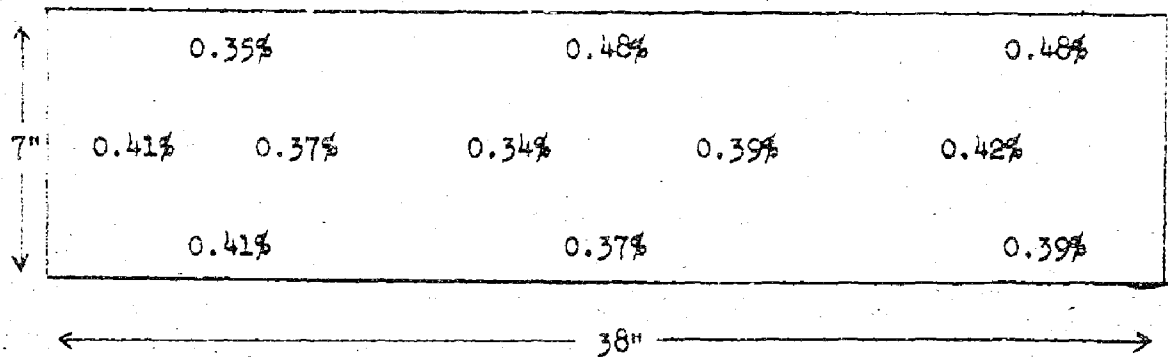
### Laminate Composition

Resin .....	V-204 (Plastics and Coal Chemicals Div., Allied Chemical Corporation)
Reinforcement .....	13 ply, 181 glass cloth
Curing Temperatures -	
"B" stage .....	3 minutes at 265°F.
Press Cure .....	30 minutes at 290°F. (200 psi)
Postcure .....	1 day at 110°C., 1 day at 150°C., 1 day at 175°C. and 1 day at 200°C.
Laminating Procedure .....	Standard dry layup



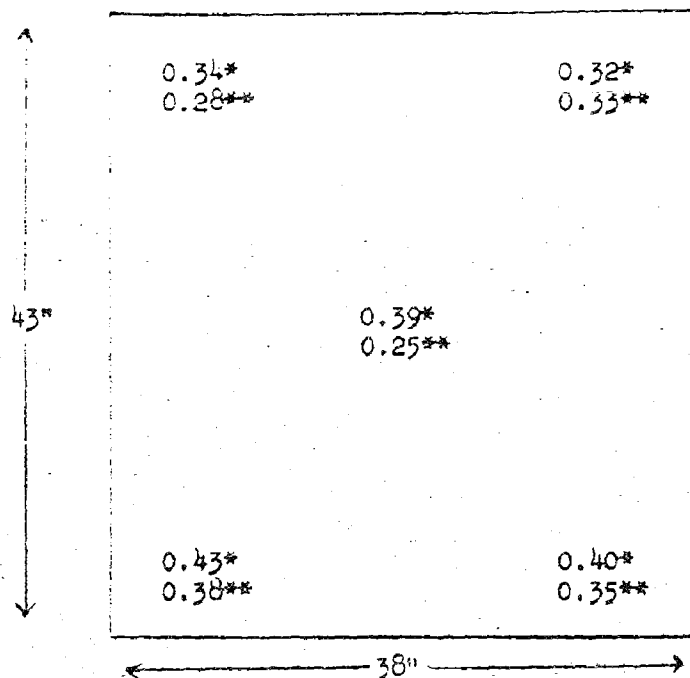
APPENDIX V

Variations in Finish Loading  
in Commercial 181-A-172 Cloth



# APPENDIX VI

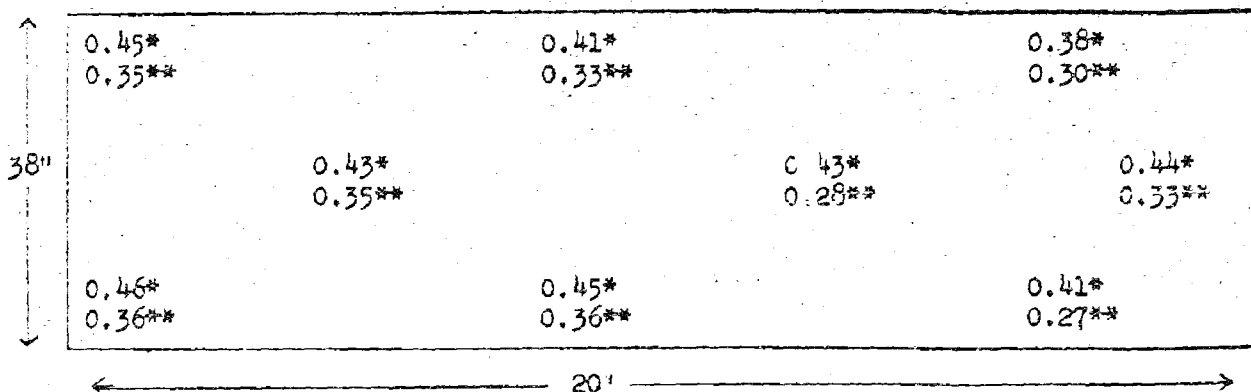
## Variations in Finish Loading in Commercial 181-A-1100 Cloth



\* % A-1100 based on % C using blank of 0.015% C

\*\* % A-1100 based on % N using blank of 0.001% N

## Commercial 181-A-1100 Cloth (Larger Sample)

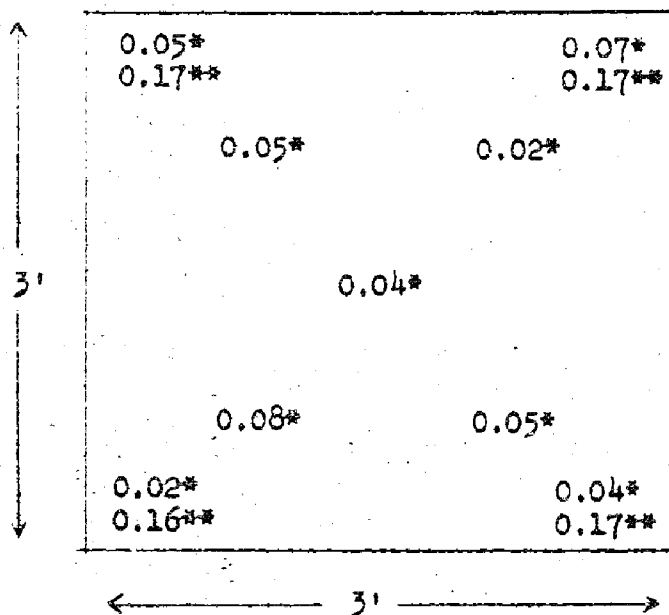


\* % A-1100 based on % C using blank of 0.015% C

\*\* % A-1100 based on % N using blank of 0.001% N

## APPENDIX VII

### Variations in Finish Loading in Commercial 181-Volan A Cloth



\* % Volan based on % C using blank of 0.015% C  
\*\* % Volan based on % Cr

APPENDIX VIII

Four-Hour Soxhlet Extraction of A-1100-Finished Cloths With Water

<u>Test Number</u>	<u>Per Cent A-1100 Loading Before Extraction</u>	<u>Per Cent A-1100 Loading After Extraction</u>	<u>Per Cent of A-1100 Finish Removed</u>
1	0.25	0.063	75.
2	0.38	0.063	84.
3	0.48	0.048	90.
4	0.73	0.11	87.
5	1.50	0.079	94.

APPENDIX IX

Volan A

<u>Cloth</u>	<u>Per Cent Chromium</u>	<u>Per Cent Volan A Based on Per Cent Chromium</u>	<u>Per Cent Carbon</u>	<u>Per Cent Volan A Based on Per Cent Carbon (0.015% C Blank Subtracted)</u>
Commercial	0.057	0.13	0.023	0.04
Commercial	0.069	0.16	0.022	0.03

## APPENDIX X

## Attempts to Prepare High Volan A Loadings on 181-112 Cloth

Prep. No.	Volan Cloth Nominal Loading and Method of Preparation	Analysis Before Soxhlet Water Extraction				Analysis After Soxhlet Water Extraction (4 days)			
		% Cr	% Volan A Based on % Cr	% C	% Volan A Based on % C	% Cr	% Volan A Based on % Cr	% C	% Volan A Based on % C
1	0.8% Volan A, heat set 5 minutes at 125°C., unwashed	0.229	0.53	0.104	0.52	0.064	0.15	0.017	0.08
2	0.8% Volan A, heat set 5 minutes at 125°C., washed one minute, dried two minutes at 125°C.	0.073	0.17	0.016	0.08	0.066	0.15	0.019	0.09
3	0.8% Volan A, heat set 20 minutes at 125°C., unwashed	0.246	0.56	0.083	0.41	0.063	0.14	0.013	0.06
4	0.8% Volan A, heat set 20 minutes at 125°C., washed one minute, dried two minutes at 125°C.	0.092	0.21	0.029	0.14	0.077	0.18	0.022	0.11

\* 0.005% Cr blank subtracted } Analysis of blank cloth  
 \*\* 0.008% C blank subtracted } before loading.

\*\*\* 0.004% Cr blank subtracted } Analysis of water  
 \*\*\*\* 0.004% C blank subtracted } extracted blank cloth



APPENDIX XI

QUALITATIVE TEST PROCEDURES

## APPENDIX XI

### Qualitative Test Procedures

Table 1

Scheme for Identifying A-1100,  
A-172, Volan and Blank Cloths

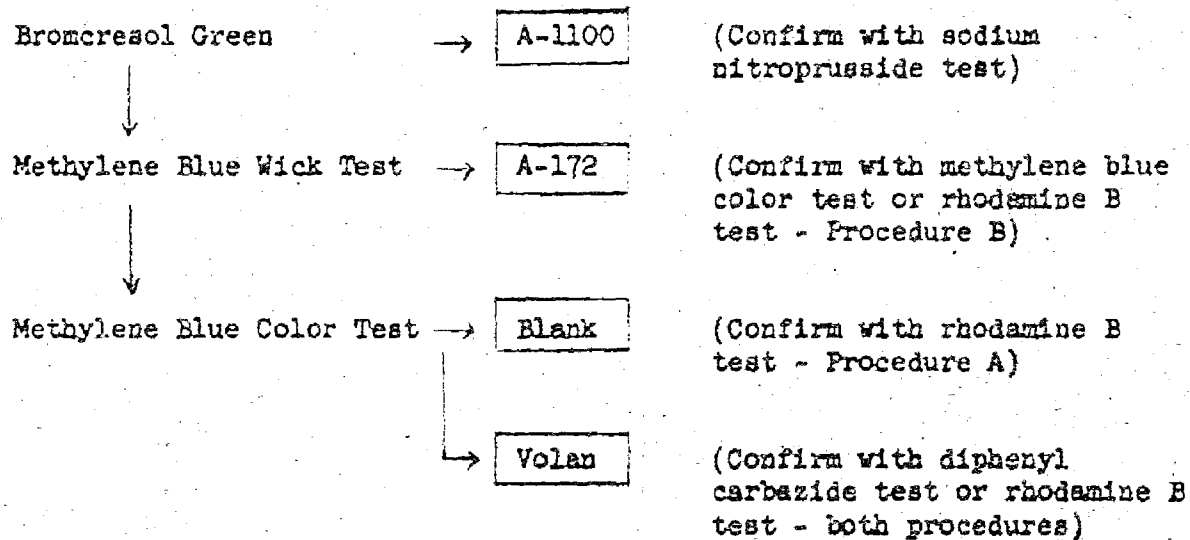


Table 2

Summary  
Colorimetric Tests for Finishes on Glass Cloth

Qualitative Test	Type of Finish		Blank* Unfinished Cloth	Time Required to Perform Test	Sensitivity
	A-1100	A-172 Vulcan			
Resorcinol Green	Blue	Colorless	Colorless	1 minute	0.1% A-1100
Sodium Nitroprusside	Violet	Colorless	Colorless	6 minutes	0.2% A-1100
Methylene Blue Wick Test	Wicks	Does not wick	Wicks	1-2 minutes	0.1% A-172
Methylene Blue Color Test	Pale blue	Medium blue	Purplish- blue	1-2 minutes	0.05% A-172 0.1% Vulcan*
Resorcinol B - Procedure A	Pink	Pink	Colorless to faint pink	5 minutes	0.05% A-172 0.1% Vulcan*
Resorcinol B - Procedure B	Pink	Pink	Colorless to faint pink	3 minutes	0.05% A-172 0.1% Vulcan*
Diphenyl Carbazide	Colorless	Colorless	Colorless	10 minutes	0.05% Vulcan*

\* No cloths of lower Vulcan A loading were available; therefore, although increased sensitivity could probably be attained, this was not established.

### BROMOCRESOL GREEN TEST:

Bromocresol green is an acid-base indicator which reacts with the amino group of A-1100-finished cloth and "dyes" this cloth blue. Volan and A-172-finished and "blank" unfinished cloths do not retain any blue color when they are "dye" with the indicator and then washed; however, inherent basicity of blank cloth (or A-172 or Volan treated) may cause the cloth to appear blue when it is removed from the bromocresol green solution. This color will immediately disappear when it is washed.

### Reagents and Apparatus:

1. Master indicator solution: 0.2% solution of bromocresol green (3', 3'', 5', 5'' - tetrabromo-2-cresolsulfonaphthaleine sodium salt) in ethanol.
2. Test solution: mix 10 ml. of the master solution with 90 ml. of distilled or demineralized water (this solution should be orange with a tinge of green).
3. 50 ml. beakers
4. Glass stirring rod with flat end
5. Wash bottle containing distilled or demineralized water

### Procedure:

1. Pour 5-10 ml. of the test solution into a clean 50 ml. beaker.
2. Cut about a one-inch square piece from the cloth to be tested and lay it in the beaker containing the test solution.
3. Using the flat end of a glass stirring rod, rub the surface of the cloth for about 10-15 minutes.
4. Pour off the dye solution, remove the cloth and rinse it well with water from the wash bottle.
5. Observe if the cloth appears to be blue.

Blue	-----	A-1100-finished cloth
Colorless	-----	Volan or A-172-finished or "blank" unfinished cloth

### SODIUM NITROPRUSSIDE TEST:

Unlike the quantitative estimation of A-1100 loadings using sodium nitroprusside, the qualitative test can be applied directly to the cloth. When this test is applied, a violet color is obtained on cloth finished with A-1100, but no color is obtained on "blank" unfinished, Volan A or A-172 finished cloth. Although this test is as specific for A-1100 finished cloth as is the bromocresol green test, it is somewhat less sensitive and more time-consuming (see Table 2) and should be used as the confirmatory test for A-1100 cloth.

#### Reagents and Apparatus:

1. 10% solution of sodium nitroprusside in water (keep solution stored in brown bottle).
2. Acetone (free of acetaldehyde)
3. 50 ml. Beakers
4. Glass stirring rod with flat end

#### Procedure:

1. Cut about a one inch square piece of the cloth and put it into a clean 50 ml. beaker.
2. Add 3 ml. of water, 1 ml. of acetone and 2 drops of the sodium nitroprusside reagent.
3. Using the flat end of the stirring rod, rub the surface of the cloth for about 10-15 seconds.
4. After 5 minutes pour off the solution, remove the cloth with tweezers and immediately observe if a violet color exists on the cloth.

Violet → A-1100 finished cloth  
Colorless → Volan or A-172 finished or "blank"  
unfinished cloth

### METHYLENE BLUE WICK TEST:

The Methylene Blue Wick Test is specific for A-172 finished glass cloths. Since the A-172 finished cloth is water repellant, it does not "wick up" a water solution of the dye, but the Volan or A-1100 treated or "blank" unfinished cloths readily absorb the dye. As low as a 0.1% A-172 loading can be detected with this test.

#### Reagents and Apparatus:

1. 0.05% Solution of methylene blue in distilled water
2. 250 ml. Beakers
3. Paper clips

#### Procedure:

1. Unwrap about 4-6 feet of the cloth from the roll and then cut a strip 1/2 in. x 4-5 in. of the cloth from this inner area; in other words, do not sample the outer wrap of the roll where it has probably been handled.
2. Attach a paper clip to one end of the specimen strip to serve as a weight.
3. Hang the cloth in a beaker and attach the other end of the strip to the rim with another paper clip. The clip used as a weight should touch the bottom of the beaker.
4. Carefully add about 50 ml. of the dye solution and with a stirring rod or spatula, push the strip against the beaker wall but do not get the dye solution on the exposed part of the strip.
5. Observe if the strip of cloth "wicks up" the dye solution in one minute. Failure to "wick" indicates A-172 finish.

#### METHYLENE BLUE COLOR TEST:

The Methylene Blue Color Test can be used to distinguish A-172 and Volan finished and "blank" unfinished cloths from each other; A-1100 treated cloth is not readily differentiable from these. Color differences among the types of cloths are most apparent when the cloths are damp; if the cloths become dry, wetting with a few drops of water will immediately restore the colors. No conclusions should be drawn on the basis of observations made on dry specimens.

When tested according to the procedure, "blank" cloth appears purplish-blue, A-172 treated cloth is medium blue (regardless of loading) and Volan A loaded cloth is light blue. A-1100 samples should not be included in this test (see Table VI); most of the dye can be washed from A-1100 treated cloth and that which remains gives the cloth a blue color which could be confused with the colors of A-172 or Volan finished cloths.

If the cloth to be tested does not wet well with the dye solution, the surface of the cloth can be rubbed with a glass stirring rod while the cloth is still in the solution in order to induce some dye to be retained; this behavior indicates A-172 finished cloth.

#### Reagents and Apparatus:

1. 0.05% Solution of methylene blue in water
2. 100 ml. Beakers

#### Procedure:

1. Dip a piece (about one inch square) of the cloth to be tested in the methylene blue solution for about 15 seconds. If necessary,

rub the surface of the cloth with a glass rod to make the cloth absorb some dye.

2. Remove the cloth with tweezers and wash off the excess dye by dipping the cloth in a beaker of water.

3. Lay the specimen on a paper towel (or some other absorbent material) and immediately observe the color of the cloth.

Purplish-blue → "Blank" untreated cloth  
Medium blue → A-172 treated cloth  
Light blue → Volan treated cloth

NOTE: Simulated, dyed specimens are located  
in a pocket of the back cover page.

*(will not be found in reproduced copies)*

#### RHODAMINE B TEST:

The Rhodamine B Test, Procedure A together with Procedure B, can be used to differentiate Volan and A-172 finished and "blank" unfinished cloths from each other. The first procedure, a modification of the Boeing Airplane Company's rhodamine B test, distinguishes "blank" cloth from Volan or A-172 finished cloth; the second procedure differentiates A-172 finished cloth from Volan A or "blank" cloth. A-1100 finished cloth cannot be distinguished by this test.

If Procedure A is used, "blank" glass cloth can be washed free (or almost free) of the pink dye which is "fixed" on it by heat, while Volan or A-172 finished cloths retain dye even after washing. In the case of Procedure B, which does not "fix" the dye on the cloth by heat, all (or almost all) of the dye can be washed from Volan treated or "blank" cloth; A-172 treated cloth, however, retains pink dye even after washing.

For both of these procedures, a piece of cloth known to be "blank" unfinished cloth should be simultaneously carried through the procedure as a control.

#### Reagents and Apparatus:

1. 0.1% Solution of rhodamine B in methanol
2. 100 ml. Beakers
3. Drying oven (at 110°C.)

#### Procedure A:

1. Cut a one inch square piece of the cloth to be tested.
2. Dip it in the dye solution for 5-10 seconds.
3. Lay it on a paper towel (or some other absorbent material) and then dry it at 110°C. for 2-3 minutes.
4. Remove it from the oven and wash off the excess dye by holding the cloth for 1-2 minutes under a strong stream of running water.
5. Carry a piece of cloth which is known to be "blank" unfinished cloth through the procedure as a control. All (or almost all) of the dye should be washed from this "blank."
6. Observe the colors of the sample and the "blank."

Colorless (or faint pink) → "Blank," untreated cloth  
Pink → Volan or A-172 treated cloth

#### Procedure B:

1. Cut a one inch square piece of the cloth to be tested.
2. Dip it in the dye solution for 5-10 seconds.
3. Remove the cloth from the solution and IMMEDIATELY wash off the excess dye by holding the cloth for 1-2 minutes under a strong stream of running water. If the NaOH from the excess dye solution is allowed to volatilize before it can be washed off, erroneous results may occur.
4. As in step 5 of Procedure A, carry a blank through the procedure. Again, it should be colorless (or almost colorless) after washing.
5. Observe the colors of the sample and the "blank."

Pink → A-172 treated cloth  
Colorless → Volan A or "blank" unfinished cloth

#### DIPHENYL CARBAZIDE TEST:

This test is the most specific, most reliable and most sensitive test for Volan finished glass cloth and should be used whenever possible. It has the disadvantage that proper facilities for handling and fuming concentrated  $\text{HClO}_4$  must be available.

When Volan A cloth is fumed with  $\text{HClO}_4$ , chromium is leached and oxidized; the chromium then is reacted with diphenyl carbazide and a colored complex is formed. Therefore, a pink color in the test solution indicates Volan A coating; "blank" unfinished and A-172 and A-1100 finished cloths yield no color with the diphenyl carbazide.



### Reagents and Apparatus:

1. 200 x 25 mm. Test tubes
2. Concentrated  $\text{HClO}_4$  (70%)
3. Diphenyl carbazide
4. Sand bath
5. Hot plate

### Procedure:

1. Cut a one-half inch square piece of cloth and put it into a clean test tube,
2. Add 2 ml. of  $\text{HClO}_4$  (about 30 drops).
3. Insert the bottom one-third of the test tube into the hot sand bath for 5 minutes. The  $\text{HClO}_4$  must fume strongly during this period.
4. Remove the tube from the sand bath and after about 1 minute cool under running water.
5. Carefully dilute the contents of the tube to 20-25 ml. with water.
6. Add solid diphenyl carbazide; a small amount from the tip of a spatula is sufficient.
7. Mix and observe; a pink color indicates Volcan A.

WARNING: Observe proper safety precautions for  $\text{HClO}_4$  in both handling and in equipment such as fume hood vents, etc.

APPENDIX XII

DETERMINATION OF CARBON IN GLASS FABRICS

LECO CARBON DETERMINATOR METHOD

## APPENDIX XII

### DETERMINATION OF CARBON IN GLASS FABRICS

#### LECO CARBON DETERMINATOR METHOD

##### I. INTRODUCTION:

Before attempting this determination, the analyst must be thoroughly familiar with the "Instruction Manual for Operation of Leco No. 515 Conductometric Carbon Determinator" and the "Instruction Manual for Operation of Leco Induction Furnaces." Principles of the method are explained in the manuals. Results should be accurate to  $\pm 0.005\%$  carbon.

The procedure described here has been used successfully to determine the amount of A-172, A-1100, or Volan finish on glass cloths.

##### II. REAGENTS AND APPARATUS:

1. Leco Induction Furnace - Model 521, 522 or 523
2. Leco No. 515 Conductometric Carbon Determinator
3. Combustion tube - Leco Catalog No. 550-120
4. Quartz enclosed carbon crucible - Leco Catalog No. 550-182
5. Tin accelerator - Leco Catalog No. 501-76
6. Iron accelerator - Leco Catalog No. 501-77
7. Crucibles - Leco Catalog No. 525-25. These crucibles are to be pre-ignited at 2300°F. in a tube furnace through which a stream of oxygen is flowing. After burning, crucibles must be handled with tongs to prevent contamination with oil from the skin; the crucibles are then stored in a desiccator.
8. Tube furnace - at 2200°F.
9. Crucible tongs
10. Tweezers
11. Desiccator
12. Variable transformer
13. A38 standard steel 166A
14. Barium hydroxide solution - see "Instruction Manual for Operation of Leco No. 515 Conductometric Carbon Determinator."
15. Cylinder of oxygen
16. Mercury

### III. PROCEDURE:

#### Directions

1. Assemble apparatus according to Figure V, "B" modification.

2. Using a quartz enclosed carbon crucible, blank out the combustion tube until a resistance of 0.5 ohms or less is obtained. Use a variable transformer to adjust the plate current to 400 ma.

3. Weigh  $1.50 \pm 0.02$  g. of iron accelerators and mix with one scoop (approximately 0.7 g.) of tin accelerator.

4. Determine a blank on the procedure by burning the iron and tin accelerators in an uncovered crucible for five minutes in a stream of oxygen.

5. Continue the oxygen purge for an additional two minutes and record resistance of the  $\text{Ba}(\text{OH})_2$  solution. Use this resistance for the first point in preparing a standard curve.

6. Run a duplicate blank.

7. Obtain three additional points for the standard curve by burning iron and tin accelerators mixed with 0.2, 0.4 and 0.7 g. of NBS standard steel 166A. Plot resistance of the  $\text{Ba}(\text{OH})_2$  solution in ohms vs. milligrams of carbon.

8. Using only tweezers to handle glass cloth, cut the sample into one-half inch pieces. Weigh 500 mg. of the cloth to the nearest milligram and place in a pre-ignited crucible.

9. Cover cloth with iron and tin accelerators, mix and burn using the same technique as used in the determination of the blank and the points for the standard curve.

#### Remarks

1. See "Instruction Manual for Operation of Leco Induction Furnaces."

2. See "Instruction Manual for Operation of Leco No. 515 Conductometric Carbon Determinator."

3. Iron accelerator contains carbon and therefore must be weighed quite accurately.

4. See remark No. 2.

6. Results should agree within 0.5 ohms.

7. Follow exactly the procedure used in steps 4 and 5. NBS standard steel 166A contains 0.027% carbon.

8. Care must be taken to prevent skin oils from contaminating glass cloth. All oil and grease must be absent from the scissors.

9. See steps 4 and 5.

10. Measure the resistance of the  $\text{Ba}(\text{OH})_2$  solution and read from the standard curve, the milligrams of carbon represented by this resistance.

11. Examine the melt in the crucible.

11. An even melt must be obtained. Discard results if pieces of unreacted glass cloth are present.

12. Calculate the per cent carbon in the sample.

$$\% \text{ C} = \frac{\text{mg. carbon (from curve)} \times 100}{\text{mg. of sample}}$$

APPENDIX XIII

EARLY METHOD FOR THE  
DETERMINATION OF CARBON AND HYDROGEN  
IN SILICON-ORGANIC COMPOUNDS

EARLY METHOD FOR  
THE DETERMINATION OF CARBON AND  
HYDROGEN IN SILICON-ORGANIC COMPOUNDS

INTRODUCTION:

The equipment, apparatus and techniques used in the determination of carbon and hydrogen in silicon-organic compounds are in most respects identical with those used in organic chemistry. There are two notable exceptions to the preceding statement: (1) In the combustion tube catalyst-filling, platinized Alfrax pellets (see "reagents") must be used to obtain complete decomposition of silicon-carbon compounds, and (2) the ignition of the silicon-organic compounds must be conducted slowly and at a low initial temperature. Low results may be expected if these exceptions are ignored.

I. Reagents:

A. Copper Oxide Catalyst:

Dissolve 60 grams copper nitrate in about 200 ml. distilled water in a porcelain evaporating dish. Add 100 grams "Aloxite" (Carborundum Company brand aluminum oxide cylindrical pellets, 3/16 in. x 3/16 in.) and evacuate under a bell jar; this draws the air out of the pores of the pellets. When the bubbles no longer erupt from the pellets, release the vacuum; the copper nitrate solution now rushes into the evacuated pores. Digest on a hot plate for one-half hour. Decant off excess liquid and dump pellets onto a wire gauze. Heat until dry, using a direct gas flame. Finally ignite in a muffle furnace at 800°C. for one hour.

B. Platinum Catalyst:

Dissolve 5 grams platinum chloride in about 75 ml. distilled water and transfer to a 300 ml. porcelain evaporating dish. Add 10 grams Aloxite pellets and complete the preparation just as was done with the copper oxide catalyst.

C. Silver Catalyst:

Prepare similarly to the platinum and copper pellets using 40 grams of silver nitrate and about 80 grams Aloxite pellets.

D. Silver Gauze:

100 mesh pure silver gauze.

E. Platinum Gauze:

100 mesh platinum gauze.

F. Cerium Oxide Catalyst:

Prepare similarly to copper oxide pellets using a saturated solution of cerium nitrate.

## G. Platinized Silica - Copper Oxide Flux:

This reagent is used with solid and liquid samples.

1. Place about 25 grams of amorphous silica in a 300 ml. evaporating dish. Drench with 5% platinum chloride and evaporate dry on a hot plate. Transfer to suitable porcelain crucibles and ignite to 1100°C. for four hours. This high ignition temperature is necessary to dehydrate completely silicic acid.

2. Ignite 25 grams 200 mesh CuO to 800°C.

Blend 1 and 2 by rolling in a large dry bottle having a metal cap.

## II. Apparatus:

### A. Combustion Tube:

The combustion tube is similar to that used for standard semi-micro combustions (1, 2); in this case we fuse together two standard fused silica combustion tubes so that the overall length is 39 inches with the conventional side-arm and end-tip. The tube is packed as follows:

1. A small plug of ignited asbestos, (1/4" long) is placed at the exit tip of the tube.
2. One inch of rolled silver gauze is placed against the asbestos plug.
3. One inch of silver catalyst pellets is placed next to (2).
4. One and one-half inch of rolled silver gauze are placed next to (3).
5. Four inches of copper oxide catalyst are placed next to (4).
6. Thirteen and one-half inches of a mixture of three parts platinum catalyst to one part cerium oxide catalyst with a few platinum stars are placed next to (5).

The silver and copper oxide section of the train is heated by a tube furnace about 8 in. long and maintained at a temperature of 550°C. The platinum section is heated by a thirteen inch tube furnace to a temperature of 1000°C. The furnaces should be touching and none of the CuO should be allowed to come into the 1000°C. zone, since CuO melts below this temperature and it would "flux" with the tube. It is better to have the platinum section lap over into the 550°C. zone slightly for safety.



### B. Absorption:

Three standard soft glass Pregl micro-absorption tubes are used. The first one which immediately follows the train is filled with indicating "Drierite" crushed to about 20 mesh and screened to remove fines. This should be done in a dry box. This tube serves to absorb water produced by combustion of hydrogen in oxygen. The second absorber, which follows the "Drierite," is for the absorption of the carbon dioxide, and it is filled with "ascarite" with a 1/4 inch layer of "Drierite."

The final absorber is filled with "Ascarite" between two equal layers of "Drierite." That is to say, "Ascarite" in the middle of the tube and "Drierite" at the ends. This final absorber is used as a tare on a double pan balance. If single pan balances, such as the Mettler or Sartorius, are used, the final absorber is weighed before and after each run and a correction is applied to the net weights of the water and carbon dioxide absorbers on this basis.

### C. Oxygen Source:

The oxygen is purified by passing through a tube furnace containing copper oxide pellets heated to 550°C. followed by absorbers containing "Ascarite" and "Drierite." This purified oxygen is then passed into a pressure regulator (Fisher 20-220) thence through a bubble counter, followed by "Drierite" and "Ascarite" absorber traps. The oxygen gas now has the relative humidity that is obtained by passing it through "Drierite," and "Drierite" is being used to absorb the water (produced by combustion of the sample) at the exit end of the tube. These conditions should always be maintained.

### D. Mariotte Bottle:

Fisher, 20-250 two liter - Micro support tripod for same Fisher 20-252. The bottle is filled with water and attached to the final absorber (1) (2).

### E. Sample Combustion Unit:

In the introduction we stressed the importance of a slow combustion at a low initial temperature. Gradually the temperature is increased to 1000°C. This method of heating can be effected by gradually raising the temperature of a burner or furnace beneath, or around the sample, or by slowly moving a high temperature tube furnace from a point beyond the sample to a point at which the furnace completely envelops the sample. In our laboratory we use a split tube-furnace mounted on a feed screw driven by a low-speed motor, such as is described by Hallet (3). The heating cycle should cover about thirty minutes.

### F. Platinum Baffle:

The platinum baffle is a one-inch coil of platinum gauze with a hook or loop on one end to facilitate removal from the train. It is placed

at the rear end of the sample boat during combustion and it acts as a reflector and catalyst and cuts down on explosion hazards.

#### PROCEDURE:

Weigh the absorption tubes and attach to the train in the correct order.

To sample solids and liquids which are stable at room temperature, proceed as follows:

##### (1) Liquids:

Half fill a porcelain micro-combustion boat with platinized silica-copper oxide flux. Weigh to  $\pm 0.02$  mg. From a capillary dropper add approximately 10 to 40 mg. liquid sample and weigh again to  $\pm 0.02$  mg. Now swing up the tip on the Mariotte bottle so as to exert a back pressure on the train. Introduce the boat containing the sample into the train, pushing it to a point within one inch of the hot catalyst. Place the platinum baffle directly behind the boat, and replace the rubber stopper in the entrance end of the combustion tube. Regulate the oxygen flow by adjusting the outlet on the Mariotte bottle so that the water is displaced from the bottle at the rate of 6 ml. per minute. Heat the sample as described under "E. Combustion Unit" in the section of this paper captioned "Apparatus." Continue flushing for an additional thirty minutes or longer, if necessary. (Occasionally a droplet of water condenses in the exit tube or in the capillary portion of the "Drierite" tube and when this occurs, an extra-long flushing period is necessary.)

##### (2) Solids:

Weigh the empty boat, add the solid sample, weigh again to obtain sample weight. Cover the sample with a layer of platinized silica-copper oxide flux and introduce to the combustion zone. Proceed from here as with a liquid.

##### (3) Glass Cloths:

For sampling glass cloths the following technique has been found satisfactory. Ignite a piece of thin platinum foil, about 1-1/2 inches long and about 3/4 inches wide. Weigh on a semi-micro balance as accurately as possible,  $\pm 0.02$  mg. Now wrap approximately 300 mgs. of the cloth sample in the platinum so that the resultant bundle assumes the shape of a cylinder. Weigh again to obtain the sample weight. Turn off the oxygen flow at the Mariotte bottle and remove the rubber stopper and platinum baffle from the combustion tube. Push the platinum foil containing the sample into the combustion zone to a spot about one inch from the hot catalyst. Place the baffle at a spot just touching the sample and replace the stopper in the combustion tube. Regulate the oxygen flow to 6 ml. per minute. Proceed as with liquids and solids.

After the flushing is complete, detach the absorbers while the oxygen continues to flow. Raise the outlet tube from the Mariotte bottle. Allow the absorbers to stand in an empty desiccator for ten minutes.

Wipe each absorption tube with a dry chamois, allow to stand in the balance case for five minutes and weigh to  $\pm 0.02$  mg.

Use white cotton gloves when handling the absorption tubes.

Calculations:

$$\% C = \frac{\text{mgs. CO}_2 \times 0.2729 \times 100}{\text{mgs. Sample}}$$

$$\% H = \frac{\text{mgs. H}_2\text{O} \times 0.1119 \times 100}{\text{mgs. Sample}}$$

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APPENDIX XIV

QUANTITATIVE DETERMINATION OF A-172 FINISH ON GLASS FABRICS

ETHYLENE EVOLUTION METHOD

## APPENDIX XIV

### QUANTITATIVE DETERMINATION OF A-172 FINISH ON GLASS FABRICS

#### ETHYLENE EVOLUTION METHOD

##### I. INTRODUCTION:

When glass fabric is finished with A-172,  $C_2H_3Si(OC_2H_4OCH_3)_3$ , the ultimate "cured finish on the glass substrate is a resinous polymer having the formula  $[C_2H_3SiO_3/2]_x$ . We have found that reaction of the finished glass with phosphoric acid gives ethylene quantitatively. The reaction on which the analysis is based is:



The ethylene is trapped on silica gel and subsequently measured by gas chromatography. Loadings calculated from this method of analysis agree well with those based on total carbon determinations. The ethylene evolution method has the added advantage of extreme sensitivity; it is possible to detect less than 0.01% A-172 finish.

Although we have said that the ultimate finish on the glass fabric is a vinylsiloxane,  $C_2H_3SiO_3/2$ , it is customary to express the loadings as weight per cent A-172; this custom is observed in the procedure described here.

A Barrrell Kromp-Tog was used in developing this procedure and the conditions described are for that instrument; obviously, other gas chromatographs would serve equally well but the optimum conditions would have to be determined for the instrument being used.

The directions in the procedure are very detailed but have been deliberately written thus to enable an inexperienced analyst to use the method.

This method is not meant to compete with the total carbon or rhodamine B methods regarding rapidity; it, on the contrary, is specific and more sensitive and is both accurate and precise.

##### II. REAGENTS AND APPARATUS:

1.  $H_3PO_4-P_2O_5$ : About 1 g.  $P_2O_5$  (Fisher Certified Reagent) per 1 ml. of 85%  $H_3PO_4$ . Carefully add the  $P_2O_5$  to the  $H_3PO_4$ . When practically cool, stopper the flask to protect the reagent from moisture.

2. Dry ice
3. Acetone
4. DC 710 Silicone oil bath
5. Cylinder of dry nitrogen with regulator
6. Cylinder of helium with regulator
7. Cylinder of ethylene
8. Silica gel - 20 x 40 mesh
9. Copper and glass  $\text{SiO}_2$  trap
10. Heating mantle - 100 ml., 50 w.
11. Variac to control heating mantle
12. Reaction flasks - about 70 ml. volume, 55 mm. diameter
13. 2 Dewar flasks: 1 - 60 mm. I.D., about 140 mm. deep  
1 - 120 mm. I.D., about 330 mm. deep
14. Burrell silicone seals, sockets and connectors
15. Burrell Xromo-Tog
16. Gas sampling system
17. Generating apparatus as shown
18. Burrell Planimeter
19. Tygon tubing

### III. PROCEDURE:

#### A. Preparation of Standard Curve for Gas Chromatography:

<u>Directions</u>	<u>Remarks</u>
1. Establish the following Xromo-Tog conditions:	
Sample cell block: 40°C.	
Detector: 100°C., 200 ma.	
Column: 2%N alumina, 14/28 mesh, 25 v., 60°C.	
He Flow: 2 lb./in. <sup>2</sup> head of pressure at the diaphragm valve, flow rate to be varied to change the retention time.	

2. Attach the gas sampling system to the Kroco-Tog.

3. Attach the cylinder of pure ethylene to the sampling system.

4. Use a calibrated 1 ml. sample bulb in the instrument sample system.

5. Check for leaks in the sampling system by evacuating the system, closing off the pump, and observing if the mercury manometer drops any in about 10 minutes.

6. Adjust the flow rate to about 74 ml./minute.

7. Enter a pressure of ethylene (about 100-200 mm.) into the sample cell and sampling system, and then re-evacuate the system. For this step the left-hand stopcock (the one nearest the sampling system) is in the horizontal position and the other (right hand) stopcock is vertical.

8. Enter a measured pressure (about 100 mm.) of ethylene into the sample cell.

9. Close off, i.e., put in vertical position, the left-hand stopcock.

10. Turn on the recorder and put the attenuation control on 2x.

11. Enter the sample into the helium stream by turning the right-hand stopcock to the horizontal position. Always turn each instrument sample cell stopcock in the same direction. For example, always have the notched side of each stopcock facing either upward or inward--never downward or outward.

12. Continue the run about 1 to 2 minutes beyond the ethylene peak.

5. In a leak-free system, the manometer should not drop.

6. This flow rate will give one point on the standard curve.

7. This is to purge the system with ethylene.

11. The position of the stopcocks used in the calibration of cell volume must be always used in the standard runs.

13. Measure the peak area and the retention time.

13. Do not forget to multiply the measured peak area times two for the attenuation.

14. Run two more pressures of ethylene in the same manner (steps 8 through 13) at the same flow rate.

15. Change the helium flow rate to about 70 ml./min. and run three more standards at this flow rate.

16. Measure the retention times and areas of these standards.

17. Change the flow rate several more times to obtain a range of retention times from about 5 min. 30 sec. to about 7 min. 30 seconds. Run three standards at each flow rate.

17. About 5-6 different retention times should suffice.

18. Calculate the mg. of ethylene per  $\text{cm}^2$  for each standard.

$$\frac{\text{mg ethylene}}{700} \times \frac{373}{(273+T)} \times \frac{\text{vol. of sample bulb (ml.)} \times 1.180}{\text{cm}^2 \text{ area}} = \text{mg/cm}^2 \text{ ethylene}$$

T = temperature in  $^{\circ}\text{C}$ . of the instrument sample cell block.

19. Plot  $\text{mg/cm}^2$  vs. retention time on linear paper. Draw a suitable curve through the points; a given point should not differ from the curve by more than  $\pm 5\%$  of the  $\text{mg/cm}^2$  factor.

20. This is then the master curve. Each day cloths are to be sampled, just a few standards need to be run as a check on technique and conditions. If these points differ from the master curve by more than  $\pm 5\%$ , more standards must be run to establish a curve for that day.

### B. Procedure for Generating Ethylene:

1. Prepare dry ice/acetone baths in both Dewars.



2. Activate and clean  $\text{SiO}_2$  trap by heating the copper tubing containing the  $\text{SiO}_2$  to about  $150^\circ\text{C}$ . with the oil bath and evacuate the trap. Close off the open stopcock before the trap is removed from the evacuating system.

3. Seal the ball joint between the condenser and the water trap with  $\text{H}_3\text{PO}_4$ .

4. Make sure the entire generating apparatus is dry ( $\text{H}_2\text{O}$  trap, condenser, flask, etc.)

5. Put a 0.5 g. sample of the cloth in the dry reaction flask.

6. Add about 10 cc. of the  $\text{H}_3\text{PO}_4 + \text{P}_2\text{O}_5$  reagent and wet the ground glass neck with it.

7. Connect the flask to the condenser and water trap assembly, using the reagent to seal the joint.

8. Purge with a fast flow of dry nitrogen for a few minutes to remove moist air.

9. Raise the dry ice/acetone bath around the water trap.

10. Turn down the stream of nitrogen to a low flow rate.

11. Attach to the water trap the "A" end of the silica gel trap which is immersed in its dry ice/acetone bath.

12. Open both stopcocks on the trap (first "A", then "B") and after equilibrium is established, attach the bubbler as shown on page . Adjust the nitrogen flow rate to 1-2 bubbles per second.

13. Raise the heating mantle around the flask and turn on the current. Use a voltage setting of 76 v.

2. Immediately after each run, a vacuum is pulled on the trap while the oil bath is still hot. Keep both stopcocks closed when the trap is not in use.

3. Do not use grease.

4. The apparatus may be dried between runs by rinsing with acetone and passing a stream of nitrogen through the system.

5. Cut the sample into small (about 1/2 inch square) pieces before putting it in the flask.

6. Make sure all the glass cloth is covered with the reagent.

11. Tygon tubing, Burrell sockets plus silicone seals and a connector are used for this connection.

13. The reaction should be carried out at a temperature of about  $300^\circ\text{C}$ .

14. Continue the heating for 30 minutes.

15. Make periodic flow rate adjustments during the reaction to keep the flow at 1-2 bubbles per second.

16. Disconnect the silica gel trap and immediately close both stopcocks. Detach the bubbler and turn off the heating mantle.

#### C. Measurement of the Ethylene:

1. Establish equilibrium for the following Xromo-Tog conditions:

Detector: 100°C., 200 ma.  
Column: 2 1/2% alumina, 14/28 mesh,  
60°C., 25 v.

He Flow Rate: 3 lb./in.<sup>2</sup> head of pressure at diaphragm valve, about 76 ml./min. adjusted with needle valve.

2. Check for leaks in the system. One method is to plug the gas flow exit and see if the flow drops to a zero reading on the flowmeter.

3. With the dry ice/acetone bath still around the silica gel trap, evacuate the trap. Attach the "B" end to the vacuum system, open stopcock "B" and evacuate about 30 seconds. Close the stopcock and remove the trap from the vacuum system and from the dry ice/acetone bath.

4. Connect the trap to the Xromo-Tog. Both stopcocks on the trap are closed at this point; on the instrument sample cell, the right-hand stopcock (closest to the column) is horizontal and the left-hand stopcock (next to the SiO<sub>2</sub> trap) is vertical.

5. Turn on the Xromo-Tog chart.

14. The first 10 minutes is to bring the flask and its contents up to temperature; the remaining 20 minutes is reaction and purge time.

16. Leave the SiO<sub>2</sub> trap in the dry ice/acetone bath.

1. Detector and column conditions must be kept constant for all samples and standards. The flow rate will drop to about 70 ml./min. when the silica gel trap is put into the system.

4. A ring stand, clamp and ring can be used to support the trap.

6. Carefully raise the silicone oil bath, which has been heated to 170-190°C., around the trap so that all the copper tubing containing the gel is in contact with the oil.

7. IMMEDIATELY open stopcock "B", stopcock "A" and then turn the left-hand instrument sample cell stopcock to the horizontal position.

8. Continue the run somewhat beyond (1 to 2 minutes) the point where the pen returns to the baseline after the ethylene peak. Attenuate the ethylene peak if necessary to keep it on scale.

9. Turn the left-hand instrument cell stopcock to the vertical position; close stopcocks "A" and "B" on the trap. Remove the trap from the Kross-Teg.

10. While the trap is still in the hot oil bath evacuate the trap. Close off the stopcock.

11. Measure the retention time and the area of the ethylene peak.

12. Using the appropriate calibration factor of mg. of ethylene per  $\text{cm}^2$  for the measured retention time, calculate the % ethylene and the % A-172 on the sample.

$$\frac{\text{cm}^2 \text{ of ethylene} \times \text{mg./cm}^2 \times 100}{\text{mg. sample}} = \% \text{ ethylene}$$

$$\% \text{ ethylene} \times 10 = \% \text{ A-172}$$

6. It is best to wipe off the "frost" that forms when the trap is removed from the dry ice/acetone bath; otherwise violent spitting occurs when the hot oil bath is raised. Do not let the trap stand around at room temperature for any long period of time before it is run.

8. The large peak at 1-2 minutes is air (or  $\text{H}_2$ ); a small ethane peak 3-4 minutes can be ignored. The retention time of the ethylene is usually between 6-7 minutes.

10. This step is to ensure that the trap is clean for the next run.

Table 3

Comparison of A-172 Loadings Determined by  
Total Carbon and Ethylene Evolution

<u>Cloth</u>	<u>% C</u>	<u>% A-172 Based On % C*</u>	<u>Per Cent Ethylene</u>	<u>% A-172 Based on % Ethylene</u>
0.1% (nominal) - Tonawanda swatch	0.012- 0.020	0.00- 0.06	0.003	0.03
0.3% (nominal) - Tonawanda swatch	0.042	0.32	0.026	0.26
0.75% (nominal) - Tonawanda swatch	0.057	0.48	0.047	0.47
1% (nominal) - Tonawanda swatch	0.068	0.62	0.049	0.49
2% (nominal) - Tonawanda swatch	0.110	1.11	0.105	1.05
2% (nominal) - Tonawanda swatch - H <sub>2</sub> O extracted	0.076	0.71	0.061	0.61
United Merchants - commercial	0.046	0.35	0.026	0.26
J. P. Stevens - Commercial	0.048	0.39	0.027	0.27
	0.054	0.46	0.027	0.27

\* 0.015% C blank subtracted

APPENDIX XV

QUANTITATIVE ESTIMATION OF A-172 LOADING ON GLASS CLOTHS

REDIAMINE B METHOD

## APPENDIX XV

### QUANTITATIVE ESTIMATION OF A-172 LOADING ON GLASS CLOTHS.

#### RHODAMINE B METHOD

##### I. INTRODUCTION:

This test is quantitative to about 0.1% loading, but it is not specific for A-172; therefore it is necessary to establish beforehand that A-172 is the only finish present on the fabric being tested.

The principle of the method depends on the ability of the rhodamine B to attach itself to the A-172 molecule (probably to the "R" group), and although it is possible to apply the dye directly to the finished cloth, the intensities of the colors so produced are not proportional to the loadings. However, if the fabric samples are ground to about 500 mesh and the resultant powders are then dyed with rhodamine B, the color intensities are then proportional to the A-172 loadings. The obvious explanation is that grinding liberates A-172 resin particles so that the dye can attach itself to them and the eye can perceive the dyed particles.

In the procedure described here, two precautions should be observed: (1) the grinding step should not be unduly prolonged, and (2) rubber gloves should be worn during the grinding and dyeing operations to protect the skin against unnecessary staining from the dye and irritation caused by any glass dust particles getting into the skin.

A one-inch-square sample of cloth is used in this procedure, and no weighing is made; we have found this to be a convenient size, but the specimen size could be varied to suit individual tastes provided, of course, that the comparison standards were prepared from the same size as the sample specimen.

##### II. REAGENTS AND APPARATUS:

1. 0.1% Solution of rhodamine B (practical, Eastman Organic Chemicals, P 4453) in methanol
2. 15 ml. Centrifuge tubes and rubber stoppers
3. Porcelain mortar and pestle
4. Fritted crucibles
5. Drying oven (110°C.)
6. Centrifuge
7. Rubber gloves

### III. PROCEDURE:

#### A. Preparation of Standards - Recommended Method:

<u>Directions</u>	<u>Remarks</u>
1. Prepare a series of cloths of various loadings from 0.0% (blank cloth) to about 1%; 0.2% A-172 intervals are desirable.	1. Instructions for loading glass fabrics with A-172 are given in Union Carbide Corporation-Silicones Division circular No. SF-1027A.
2. Chemically analyze these cloths by using the Gas Chromatographic Method for the determination of the ethylene generated by reaction of A-172 treated cloth with $H_2PO_4 + P_2O_5$ , or by a total carbon determination.	
3. Cut a one inch square from the same area which was sampled for chemical analysis; cut each square into about four parts.	
4. Unweave the four parts by pulling the fibers apart with tweezers. Put these fibers into a clean porcelain mortar.	
5. Grind the fibers until a powder is just obtained, i.e., no distinct fibers should be visible. DO NOT GRIND MORE THAN NECESSARY TO REACH THIS POINT.	5. The grinding technique that is used must be reproduced for all samples and standards.
6. Transfer the powder as quantitatively as possible to a dry centrifuge tube.	6. A small funnel aids transfer.
7. Repeat steps 4-6 for each standard.	7. Clean the mortar and pestle between standards (or samples) by grinding a few grams of sea sand briefly, then washing and wiping thoroughly.
8. Proceed with section III-D, the Dye Test.	

#### B. Preparation of Standards - Alternate Method:

1. Cut about a six inch square piece of blank cloth into small pieces (about 1/2 inch square).

2. Unweave about six of these pieces and put the fibers in a clean porcelain mortar.

3. Grind the fibers as described in section III-A, step 5.

4. Transfer the powder to a small bottle or jar.

5. Repeat steps 2, 3 and 4 until all the small pieces of the blank cloth are ground.

6. Cut into small pieces (about 1/2 inch square) about a six inch square piece of A-172, homogeneously, heavily (about 1%) loaded cloth which has been chemically analyzed.

7. Repeat steps 2, 3, 4 and 5 and put the powder in another bottle or jar.

8. Make up mixtures (200 mg. total) of the "blank" powder and the A-172 loaded powder so as to simulate the following A-172 loadings on the mixtures: 0.0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%. The remainder of the blank and A-172 powders is reserved for future use.

9. Transfer quantitatively each mixture to a dry centrifuge tube.

10. Proceed with section III-B, the Dye Test.

#### C. Preparation of Samples:

Prepare samples in the same manner as described for the standards in section III-A, steps 3 through 8.

6. If the swatch from which the six inch square was taken is not homogeneously loaded, representatively sample a single area for both chemical analysis and dye tests.

7. Clean the mortar and pestle by grinding in it some blank cloth. Discard the powder and wipe the mortar and pestle with tissues.

8. For example, if 80 mg. of 1% A-172 powder is mixed with 120 mg. of blank, a 0.4% A-172 standard is obtained.

It is best to run duplicate samples of the cloth to reduce the possibility of error due to heterogeneous loading.



#### D. Dye Test:

1. To each sample and standard, add about 4 ml. of the rhodamine B reagent; stopper and shake the tubes well for 1 to 2 minutes.

2. Remove stoppers and rinse down the walls of each tube with about another 1 ml. of reagent.

3. Wait about 4 minutes then centrifuge about 1 minute.

4. Carefully remove the supernatant liquid without disturbing the powder.

5. Add about 12 ml. of water to each and stir well. Centrifuge and again remove the supernatant liquid.

6. Repeat this washing step until the water wash is essentially colorless.

7. Transfer the washed, wet powder to a clean fritted crucible with a stream of water. Use suction on the crucible to remove most of the water.

8. Dry the powder on the frit at about 110°C, for about 10 minutes (or until the powder is dry). Cool the frit.

9. Compare the intensity of pink color of each sample with those of the standards in either of the following ways or in any other way which would make differences in colors more apparent to the operator: (a) by leaving the powder on the frit and finding the standard which most closely matches a given sample; or (b) by scraping the dry powders from the frits, transferring them to pieces of white paper and then matching the sample powders with the standards.

1. Since the rhodamine B color seems to fade somewhat with time, 1 or 2 standard should be run with each sample or group of samples as a check on technique and on the validity of the master series of standards.

5. A long, pointed aluminum spatula works well as a stirrer.

6. About four washings are usually necessary to remove the excess reagent.

9. In any case, a white background seems advantageous for comparing the colors.

(b) The pink stain on the fritted crucibles can be removed with methanol.

10. The % A-172 of the standard which most closely resembles the sample is then the % A-172 on the sample.

WADD TR 60-318

APPENDIX XVI

QUANTITATIVE ESTIMATION OF A-1100 LOADING ON GLASS CLOTHS

SODIUM NITROPRUSSIDE COLORIMETRIC TEST

## APPENDIX XVI

### QUANTITATIVE ESTIMATION OF A-1100 LOADING ON GLASS CLOTHS:

#### SODIUM NITROPRUSSIDE COLORIMETRIC TEST

##### I. INTRODUCTION:

This method depends on the ability of sodium nitroprusside,  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ , to form a characteristically colored product with primary amines(1). It is apparently not necessary for the A-1100 (or its hydrolysis-condensation product  $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_3/2$ ) to be in solution for the reaction to take place; it is necessary that the amino groups be exposed, or available, to the nitroprusside; and this can be accomplished precisely by grinding the A-1100 finished cloth to a powder before making the test.

Under the conditions described here, no reaction takes place between sodium nitroprusside and A-172, Volan A, "blank" glass cloth, or secondary amines, (which we have never found in A-1100 finished cloth). (By modifying the reagent, a test can be made for secondary amine.)

The violet color produced with primary amine and sodium nitroprusside is unstable; therefore, it is not possible to prepare permanent reference color standards in this manner. A series of simulated nitroprusside-A-1100 colored specimens which correspond to a range of loadings is shown on page 4.

##### II. REAGENTS AND APPARATUS:

1. 10% Solution of sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  in water (keep stored in brown bottle)
2. Acetone (free of acetaldehyde)
3. Porcelain mortar and pestle
4. Porcelain evaporating dishes - Sire 000

##### III. PROCEDURE:

###### A. Preparation of Standards - Recommended Method:

<u>Directions</u>	<u>Remarks</u>
1. Prepare a series of cloths of various loadings from 0.0% to about 1.0%; 0.2% A-1100 intervals are desirable.	1. See Union Carbide Corporation-Silicone Division leaflet SP-1034B.

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(1) Cheronis, N. D., and Entzikin, J. B., "Semimicro Qualitative Organic Analysis", p. 134, Thomas Y. Crowell Company, New York, 1947.

2. Chemically analyze these cloths by determining the per cent nitrogen by the fusion method.

3. Cut a one inch square piece from the cloth and then cut the piece into about four parts.

4. Unweave the four pieces by pulling apart the bundles of fibers with tweezers. Put these fibers in a clean porcelain mortar.

5. Grind the fibers until a powder is just obtained; i.e., no distinct fibers should be visible. DO NOT GRIND MORE THAN NECESSARY TO REACH THIS POINT.

6. Transfer the powder as quantitatively as possible to a porcelain evaporating dish.

7. Repeat steps 4 to 6 for each standard.

8. Proceed with section D, the Dye Test.

2. Fusion method is described in Union Carbide Corporation-Silicones Division Leaflet 3F-1096B.

5. The grinding technique that is used must be reproduced for all samples and standards.

7. Clean the mortar and pestle by grinding a few grams of sea sand for about one minute and wiping dry; this should be done after grinding each sample other than the blank.

#### B. Preparation of Standards - Alternate Method:

1. Cut about a six inch square piece of blank cloth into small pieces (about 1/2 inch square).

2. Unweave about six of these pieces and put the fibers in a clean mortar.

3. Grind the fibers as outlined in section III-A, step 5.

4. Transfer the powder to a small bottle or jar.

5. Repeat steps 2, 3 and 4 until all the small pieces of the blank cloth are ground.

6. Cut into small pieces (about 1/2 inch square) about a six inch square piece of A-1100, homogeneously, heavily (about 1%) loaded cloth which has been chemically analyzed.

7. Repeat steps 2, 3, 4 and 5 and put the powder in another bottle or jar.

8. Prepare mixtures (200 mg. total) of the "blank" powder and the A-1100 loaded powder and the A-1100 loaded powder so as to simulate the following A-1100 loadings: 0.0, 0.2, 0.4, 0.5, 0.8 and 1.0% A-1100. The remainder of the blank and A-1100 powders is reserved for future use.

9. Transfer quantitatively each mixture to an evaporating dish.

10. Proceed with section D, Dye Test.

#### C. Preparation of Samples:

1. Cut a one inch square piece of cloth (about 200 mg.) from the swatch, and cut this piece into about four parts.

2. Unweave these pieces and put the fibers in a clean mortar.

3. Grind as outlined in step 5, section III-A, under Preparation of Standards.

4. Transfer the powder as quantitatively as possible to an evaporating dish.

5. Proceed with Section D, the Dye Test.

#### D. Dye Test:

1. To each sample and standard add 3 ml. of water, 0.5 ml. (about 25 drops) of acetone, and 2 drops of sodium nitroprusside solution.

6. If the swatch from which the six inch square was taken is not homogeneously loaded, representatively sample a single area for both chemical analysis and dye tests.

7. Clean the mortar and pestle as directed in Remarks A-7.

8. For example, if 80 mg. of 1% A-1100 powder is mixed with 120 mg. of blank powder, a 0.4% A-1100 standard is obtained.

1. It is best to run duplicate samples of the cloth to reduce the possibility of error due to heterogeneous loading.

1. Since the violet sodium nitroprusside color is not stable, standards must be tested along with each sample or group of samples.

2. Mix well and allow to stand about 5 minutes.

3. Remove as much as possible of the supernatant liquid.

4. Immediately, (before the powders themselves become dry), compare the intensity of violet color of the samples with those of the standards.

3. A medicine dropper can be used to remove most of the liquid; a piece of filter paper can then be used to draw up the remainder.

4. Loadings may be determined more closely by estimating the loading to fall between two successive standards, e.g., between 0.4 and 0.6, is therefore 0.5%.

NOTE: Simulated Nitroprusside - A-1100 Colored Specimens are located in a pocket of the back cover page.

*(will not be found in reproduced copies of this report.)*



### I. INTRODUCTION:

A reliable indication of the silicone coating on glass fibers and cloths which have been treated with A-1100 can be obtained by determining the nitrogen content of the coated materials.

Since the A-1100 is a primary amino compound, it would appear most straightforward to titrate the amino group with acid; however, results obtained by this method have lacked precision and have generally been low. There are indications that some of the nitrogen escapes detection by the classic Kjeldahl method. A modified Kjeldahl method employing preliminary attack with HF has given satisfactory results, but the analysis cannot be completed in less than three hours.

A method is described herein where the sample is fused with dry KOH to distill the N off as  $\text{NH}_3$  into boric acid "catch solution," where it is subsequently titrated. An analysis can be completed in about one hour and ten minutes.

### II. APPARATUS:

- (a) Analytical balance - sensitive to  $\pm 0.1$  mg.
- (b) J. Lawrence Smith nickel crucible, 17 ml. capacity (Harshaw Scientific, Cat. No. H-17790). An iron crucible with approximately the same dimensions can be used.
- (c) Vycor test tube, 75 ml. capacity (Corning Glass Works, Cat. No. 19800, 25 mm. x 200 mm.).
- (d) No. 4 rubber stopper with two holes.
- (e) Ignited asbestos.
- (f) Kjeldahl connecting bulb, 52 mm. diameter (Kimble Glass Co., Cat. No. 15055).
- (g) Glass tubing (inside diameter should be less than 5 mm.).
- (h) Ring stand.
- (i) Pot furnace\* (Fisher Scientific Co., No. 6-695).
- (j) Variable transformer\*\* (Fisher Scientific Co., Cat. No. 6-700).

\* Hoskins Electric Furnace - Approximate Cost - \$55.

\*\* Approximate Cost - \$25.50.

(Both items are available from Fisher Scientific Co. under the designated catalog numbers.)



- (k) Tygon Tubing.
- (l) Erlenmeyer flask, 250 ml.
- (m) Graduated cylinder, 10 ml.
- (n) Asbestos or Transite collar.
- (o) Calibrated buret, 50 ml.
- (p) Desiccator.
- (q) Source of compressed air.

Assemble apparatus as shown in sketch.

### III. REAGENTS:

All reagents are analytical grade.

- (a) Potassium hydroxide pellets.
- (b) Distilled or demineralized water.
- (c) Boric acid solution - dilute 10 ml. of a saturated boric acid solution to approximately 50 ml.
- (d) N-100 Hydrochloric acid solution.
- (e) Methyl red indicator (dimethylaminoazobenzene -o- carboxylic acid) - 0.1 gm. in 100 ml. 60% ethanol.
- (f) Nitrogen or argon gas.

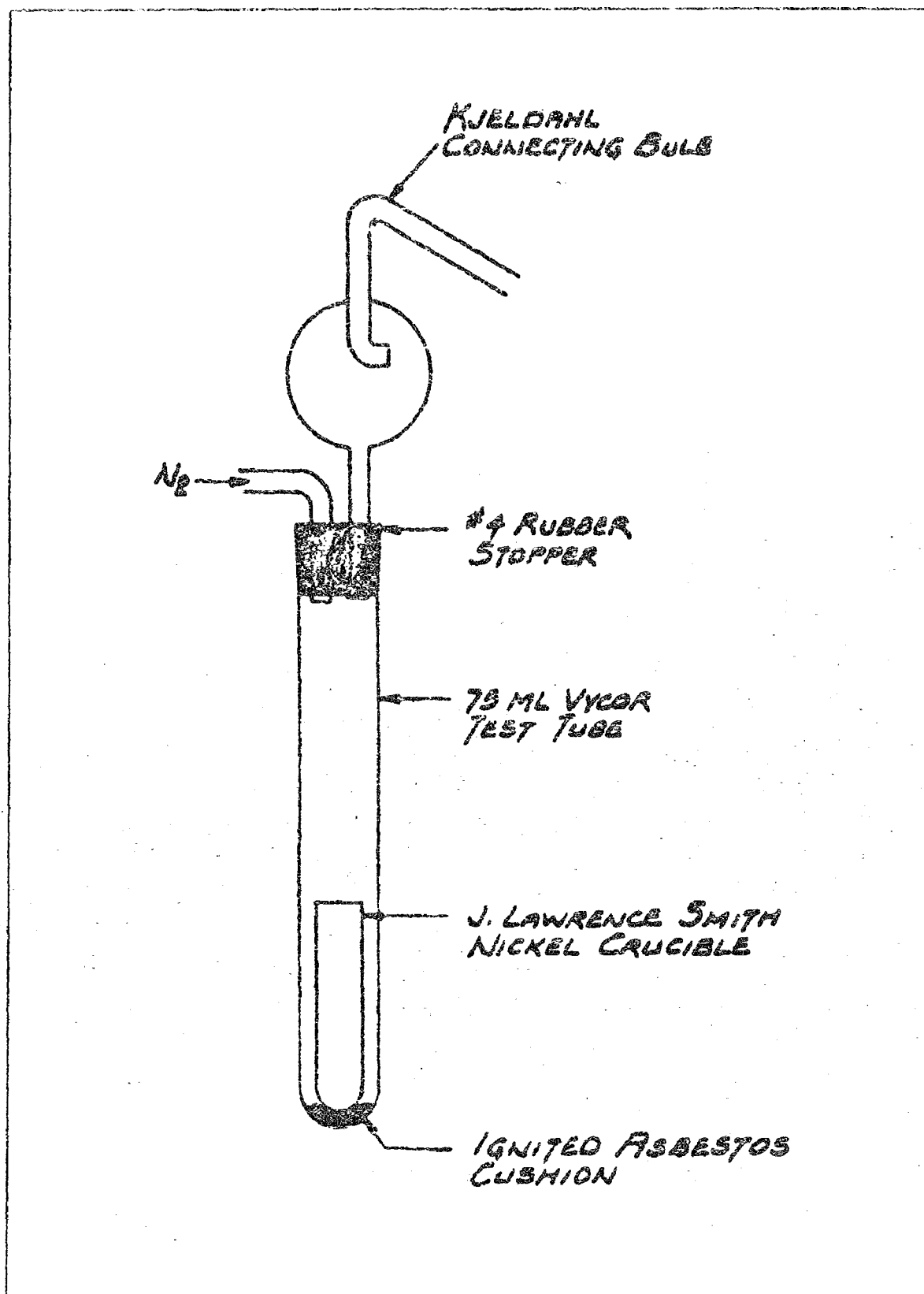
### IV. PROCEDURE:

- (1) Ignite the iron crucible and Vycor tube (containing an asbestos cushion) at 1000°C. for 5 minutes.
- (2) Cool both in a desiccator.
- (3) Weigh out accurately a 1 to 2 gram representative sample of finished glass cloth into the J. Lawrence Smith crucible.
- (4) Cover the sample with about 3 grams of KOH pellets.
- (5) Transfer the crucible to the Vycor tube and place the stopper containing the Kjeldahl connecting bulb and N<sub>2</sub> inlet tube in the position shown on the diagram.
- (6) Mount the assembly on a ring stand with the bottom 2/3 of the Vycor tube dipped into a cold pot furnace. Connect the pot furnace to a variable transformer.
- (7) Connect the exit end of the Kjeldahl bulb to a glass delivery tube with a piece of Tygon tubing. The tubing should be at least 2 feet long; this should prevent the boric acid solution from being sucked back into the Kjeldahl bulb.

- (8) Dip the delivery tube into a 250 ml. Erlenmeyer flask.
- (9) Add 50 ml. of the boric acid solution and 3 drops of the methyl red indicator to the flask. (The solution should be faintly pink.)
- (10) Connect the inlet tube to a nitrogen cylinder and adjust the flow of nitrogen so that about one bubble per second comes through the delivery tube in the boric acid solution.
- (11) Shield the upper part of the tube from the radiated heat with an asbestos collar which fits on top of the pot furnace.
- (12) Direct a jet of compressed air on the rubber stopper to keep it from becoming too hot.
- (13) Switch on the transformer and increase the voltage over a period of 20 minutes (slowly at first) until the temperature of the pot furnace is around 500°C. Temperature should not exceed 600°C., as some carry over of potassium may occur. The KOH will be reacting vigorously with the sample.
- (14) After 30 minutes the boric acid solution should be yellow. Titrate the ammonium borate in the Erlenmeyer flask to a faint pink with N/100 HCl, keeping the system connected all the while.
- (15) Continue the heating - purging - distilling operation for 5 minutes more. If the reaction is complete, the solution will remain pink; if it is not complete, more  $\text{NH}_3$  will distill over and the solution will turn yellow again. In any case, an additional 20 minutes should complete the operation.
- (16) Disconnect the tubing from the Kjeldahl flask and wash the inside of the tubing with distilled water. Add these washings to the borate solution; if the solution turns yellow titrate to a faint pink with N/100 HCl.
- Run a blank on untreated substrate. Subtract the nitrogen found in the blank from the nitrogen found in the sample to obtain the nitrogen in the A-1100 on the substrate (see calculations 1 through 3). The nitrogen in A-1100 is then converted to per cent A-1100 on substrate (see calculation 4).

#### V. CALCULATIONS:

- (1) 
$$\frac{(\text{ml. of HCl} \times \text{N of HCl for sample})}{\text{sample wt. in grams}} \times 100 \times 0.014 = \% \text{ N in sample} = A$$
- (2) 
$$\frac{(\text{ml. of HCl} \times \text{N of HCl for blank})}{\text{wt. of untreated blank sample in grams}} \times 100 \times 0.014 = \% \text{ N in blank} = B$$
- (3) 
$$A - B = \% \text{ N due to A-1100 on substrate} = C$$
- (4) 
$$C \times \frac{221}{14} = \% \text{ A-1100 on substrate}$$



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APPENDIX XVIII

QUANTITATIVE DETERMINATION OF VOLAN A

ON GLASS FABRICS: FUSION METHOD

AND PERCHLORIC ACID METHOD

## APPENDIX XVIII

### QUANTITATIVE DETERMINATION OF VOLAN A

#### ON GLASS FABRICS: FUSION METHOD

#### I. INTRODUCTION:

A procedure is described here in which the sample is fused directly with sodium carbonate. No separations are necessary and an analysis can be completed in 35 minutes.

This method is based on the assumption that the chromium content of the fabric is an accurate indication of the Volan A content of the fabric.

Accuracy of the chromium determination is about  $\pm 0.005\%$ ; implied accuracy of Volan A estimation is  $\pm 0.01\%$ .

#### II. REAGENTS AND APPARATUS:

1. Anhydrous  $\text{Na}_2\text{CO}_3$
2. Dilute (1-1)  $\text{H}_2\text{SO}_4$
3. 2.5%  $\text{KMnO}_4$  in water
4. Concentrated  $\text{HCl}$
5. Standard 0.005N ferrous ammonium sulfate solution
6. Standard 0.02N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution: 0.9807 g.  $\text{K}_2\text{Cr}_2\text{O}_7$  per liter
7. o-Phenanthroline (ferrous complex) indicator
8. 50 ml. Platinum crucible and cover
9. 10 ml. Buret
10. 50 ml. Buret
11. 250 ml. Beakers, watch glasses and stirring rods
12. Meker burner
13. Nichrome tongs
14. Tripod and wire triangle

#### III. PROCEDURE:

<u>Directions</u>	<u>Remarks</u>
1. Cut about a 2 in. square piece of cloth into small pieces (about 1/4 inch square).	1. Small pieces will fuse more easily.

2. Weigh 1 g. of these small pieces and transfer them to a clean, dry platinum crucible.

3. Weigh 7-8 g. of anhydrous  $\text{Na}_2\text{CO}_3$ . Put about one-half of this in the crucible and mix with the pieces of cloth; then pour the other half on top making sure all the cloth is covered.

4. Begin the fusion slowly by rotating the crucible (without cover) in the flame of a Meeker burner and allowing the flame to strike only the sides of the crucible. As the fusion temperature is reached, gradually heat the entire crucible to redness and set it on the wire triangle with the burner positioned under it. Cover the crucible and maintain red heat for another 5 minutes.

5. Remove the crucible from the flame and cool.

5. If the melt is rolled onto the sides of the crucible as it is cooled, it will leach more rapidly.

6. Rinse off the outside of the crucible and put it and its cover into a 250 ml. beaker; add 25 ml. of water. Slowly add portions (25 ml. total) of 1-1  $\text{H}_2\text{SO}_4$  -- wait for the reaction to subside between additions.

7. When the melt has been leached from the crucible, remove the crucible (and its cover) from the beaker and rinse it with water.

8. Dilute the contents of the beaker to about 100 ml. and cover.

9. Heat to boiling. Add 2.5%  $\text{KMnO}_4$  dropwise until a dark purple color remains.

9. This is to make sure all the chromium is as  $\text{Cr}^{+6}$ .

10. Continue the boiling for about 3 minutes.

11. Add concentrated  $\text{HCl}$  dropwise to reduce the excess  $\text{KMnO}_4$ . Continue the boiling for about 1 minute.

12. Cool the beaker and contents while bubbling nitrogen through the solution to remove any chlorine.

13. Add 20 ml. of 1-1  $H_2SO_4$  and one drop of o-phenanthroline indicator.

14. Using a 10 ml. buret, titrate with standard  $Fe^{++}$  solution to a salmon pink endpoint.

12. A water bath can be used to hasten cooling.

14. To standardize the  $Fe^{++}$  solution, pipet 10 ml. of the  $K_2Cr_2O_7$  solution into 60 ml. of water and add 40 ml. of 1-1  $H_2SO_4$  and one drop of o-phenanthroline indicator. Using a 50 ml. buret, titrate to a salmon pink endpoint.

$$N Fe^{++} = \frac{0.2}{(ml. titration + 0.06*)}$$

15. Carry a blank on all reagents through the whole procedure.

16. Calculate % Cr and % Volan A

$$\frac{[(ml_s + 0.06*) - (ml_B + 0.06*)] \times 0.01734 \times N Fe^{++} \times 100}{g. sample} = \% Cr$$

$\% Cr \times 2.29 = \% Volan A$

s = titration of sample

B = titration of blank

\* = indicator blank

QUANTITATIVE DETERMINATION OF VOLAN A  
ON GLASS FABRICS. PERCHLORIC ACID METHOD

I. INTRODUCTION:

This is a titrimetric method for total chromium; the Volan A loading is calculated from the chromium on the assumption that all the chromium is present as a compound of empirical formula  $C_4H_5O_7Cr_2$ .

The analyses obtained by this method are reproducible to 0.005% Cr, or 0.01% Volan A. The method is straightforward, employs no unique equipment and requires no unusual talent.

To those unfamiliar with perchloric acid, it should be pointed out that it should not be used in fume hoods which are customarily used for organic vapors or liquids. No danger is involved in the reaction as described here, since the quantity of organic material reacting with the perchloric acid is very small; but this method should not be applied to the analysis of Volan (the alcoholic solution of the chromium methacrylate).

II. REAGENTS AND APPARATUS:

1. 100 ml. Platinum dishes
2. 25 ml. Buret
3. 250 ml. Beakers, watch glasses, stirring rods, hot plate
4. Concentrated  $HClO_4$  70%
5. Dilute (1-1)  $H_2SO_4$
6. Concentrated  $HCl$
7. 2.5%  $KMnO_4$  in water
8. Standard 0.02N  $K_2Cr_2O_7$  solution: exactly 0.9807 g.  $K_2Cr_2O_7$ /liter
9. Standard 0.01N ferrous ammonium sulfate
10. o-Phenanthroline (ferrous complex)
11. Hydrofluoric acid
12. Wash bottle

III. PROCEDURE:

<u>Directions</u>	<u>Remarks</u>
1. Weigh 2 g. of the Volan finished cloth.	



2. Cut sample into small pieces (about 1/2 in. square) and put into a clean platinum dish.

3. Add 10 ml. concentrated  $\text{HClO}_4$ .

4. Add increments of HF to dissolve the cloth; the first HF is added dropwise, then, as the reaction becomes less violent, it is added in 1-2 ml. amounts.

5. When no further reaction takes place as the HF is added, carefully place the dish on a sand bath and evaporate the excess HF.

6. If pieces of cloth can still be seen, remove the dish from the sand bath, cool somewhat and add another couple ml. of HF.

7. Return the dish to the sand bath, evaporate the excess HF and continue the heating until strong fumes of  $\text{HClO}_4$  appear.

8. Increase the temperature of the sand bath; after a couple minutes cover the dish with a watch glass and continue to let the  $\text{HClO}_4$  fume for about 20 minutes.

9. Remove the dish from the sand bath, cool and quantitatively wash the contents into a 250 ml. beaker. Dilute to 100 ml. with water.

10. Add 10 ml. of 1-1  $\text{H}_2\text{SO}_4$ ; heat to boiling.

11. Add 2.5%  $\text{KMnO}_4$  solution dropwise until a dark purple color remains. Continue the boiling for about 10 minutes and maintain the 100 ml. volume by adding water.

12. Add concentrated HCl dropwise to reduce the purple  $\text{KMnO}_4$  color and continue boiling for 5 minutes.

13. Cool. Add 20 ml. of 1-1  $\text{H}_2\text{SO}_4$ .

3. Cover all the cloth with the  $\text{HClO}_4$ .

4. A total of about 5-10 ml. of HF is necessary.

5. Control the temperature of the sand bath to keep the solution somewhat below boiling.

8. The yellow color of the fuming  $\text{HClO}_4$  is due to oxidized chromium.

11. This is to insure complete oxidation of chromium to the hexavalent state.

12. About 5-10 drops are usually necessary.

13.  $\text{CaSO}_4$  precipitates but does not interfere with the titration.

14. Add 1 drop of  $\alpha$ -phenanthroline (ferrous complex) and stir the solution until the red precipitate dissolves.

15. Titrate to a salmon pink endpoint with standard 0.01N ferrous ammonium sulfate.

15. To standardize the ferrous ammonium sulfate, pipet 10 ml. of the standard  $K_2Cr_2O_7$  solution into 100 ml. of water; make 20% in  $H_2SO_4$ , add 1 drop of indicator and titrate to a salmon pink endpoint.

$$\text{Normality Ferrous} = \frac{0.2}{(\text{ml Ferrous} + 0.13*)}$$

16. Carry a blank on all reagents through the entire procedure.

17. Calculate the % Cr and the % Volan A on the sample.

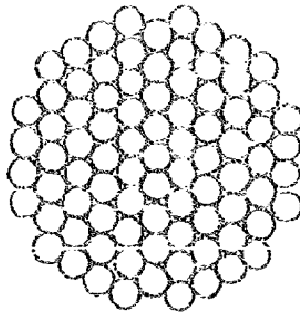
$$\frac{[(\text{ml S} + 0.13*) - (\text{ml B} + 0.13*)] \times N \text{ Fe}^{++} \times 0.01734 \times 100}{\text{g. spl.}} = \% \text{ Cr}$$

$$\% \text{ Cr} \times 2.29 = \% \text{ Volan A}$$

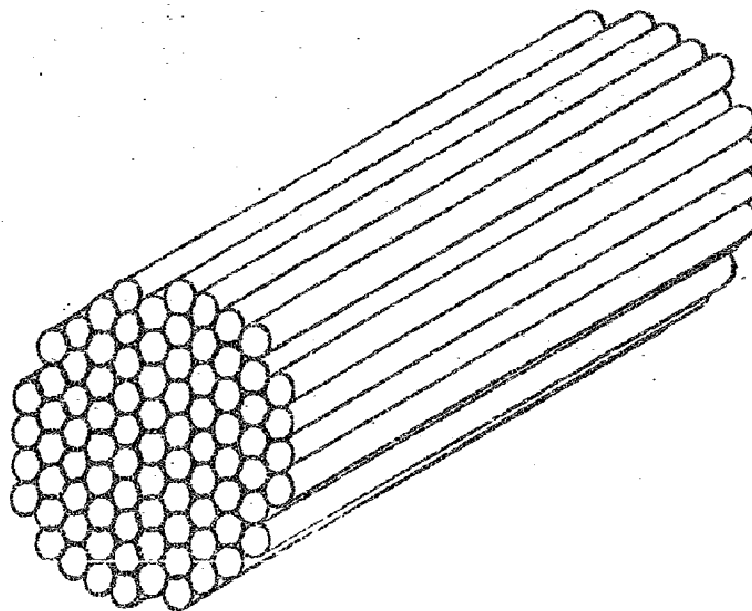
S = titration of sample

B = titration of blank

\* = indicator blank



CROSS SECTION OF GLASS STRAND



LENGTHWISE VIEW OF GLASS STRAND  
SHOWING CORRUGATED SURFACE CHARACTER

Calculation of A-172 Loading From Electron Micrograph

1. Measure the length and width of the field on the photograph and calculate in square centimeters the area using the appropriate magnification factor.
2. Count the number of hemispheres of polymer in the field and measure their diameter using a focusing magnifier. If the hemispheres are roughly the same size, an average diameter can be used.
3. Calculate in cubic centimeters the volume of the hemispheres by multiplying the number of hemispheres times  $\frac{2}{3} \pi r^3$ . Do this for each size of hemisphere.
4. Calculate the weight of the  $\text{CH}_2 = \text{CHSiO}_2/n$  by multiplying the total volume of the hemispheres times the density of the polymer, 1.2 g/cm<sup>3</sup>.
5. Calculate the per cent A-172 according to the equation:

$$\frac{\text{weight in g. } 1.7 \times 10^3 \text{ cm}^2 \text{ surface area/g.} \times 3.54^* \times 100}{\text{area of field in cm}^2} = \% \text{ A-172}$$

Sample Calculation:

$$\begin{aligned} &66,500 \times \\ &1 \text{ mm} = 0.015 \text{ micron} \end{aligned}$$

a. Field: 180 mm. by 177 mm.

$$\begin{aligned} \text{Area: } &180 \text{ mm.} \times 0.015 \text{ micron/mm} \times 177 \text{ mm.} \times 0.015 \text{ micron/mm.} \\ &= 7.16 \text{ square microns or} \\ &7.16 \times 10^{-8} \text{ cm.} \end{aligned}$$

b. Particle Count:

<u>No of Hemispheres</u>	<u>Diameter in Microns</u>	<u>Radius in Centimeters</u>
5	3.0 mm x 0.015 = 0.045	$2.2 \times 10^{-6}$
37	4.0 mm x 0.015 = 0.06	$3.0 \times 10^{-6}$
2	5.0 mm x 0.015 = 0.075	$3.5 \times 10^{-6}$
13	6.0 mm x 0.015 = 0.09	$4.5 \times 10^{-6}$

\*  $3.54 (\text{CH}_2 = \text{CHSiO}_2/n) = \text{A-172}$

3. Volume:

$$\begin{aligned}
 5 \times \frac{2}{3} \times 3.14 \times (2.2 \times 10^{-6})^3 &= 0.11 \times 10^{-15} \text{ cm}^3 \\
 37 \times \frac{2}{3} \times 3.14 \times (3.0 \times 10^{-6})^3 &= 2.09 \times 10^{-15} \text{ cm}^3 \\
 2 \times \frac{2}{3} \times 3.14 \times (3.8 \times 10^{-6})^3 &= 0.22 \times 10^{-15} \text{ cm}^3 \\
 13 \times \frac{2}{3} \times 3.14 \times (4.5 \times 10^{-6})^3 &= \frac{2.47 \times 10^{-15} \text{ cm}^3}{4.89 \times 10^{-15} \text{ cm}^3}
 \end{aligned}$$

4. Weight:

$$4.89 \times 10^{-15} \text{ cm}^3 \times 1.2 \text{ g/cm}^3 = 5.86 \times 10^{-15} \text{ g.}$$

5. Per cent A-172:

$$\frac{5.86 \times 10^{-15} \text{ g.} \times 1.73 \times 10^3 \text{ cm}^2/\text{g.} \times 3.54 \times 100}{7.16 \times 10^{-6} \text{ cm}^2} = 0.05\% \text{ A-172}$$

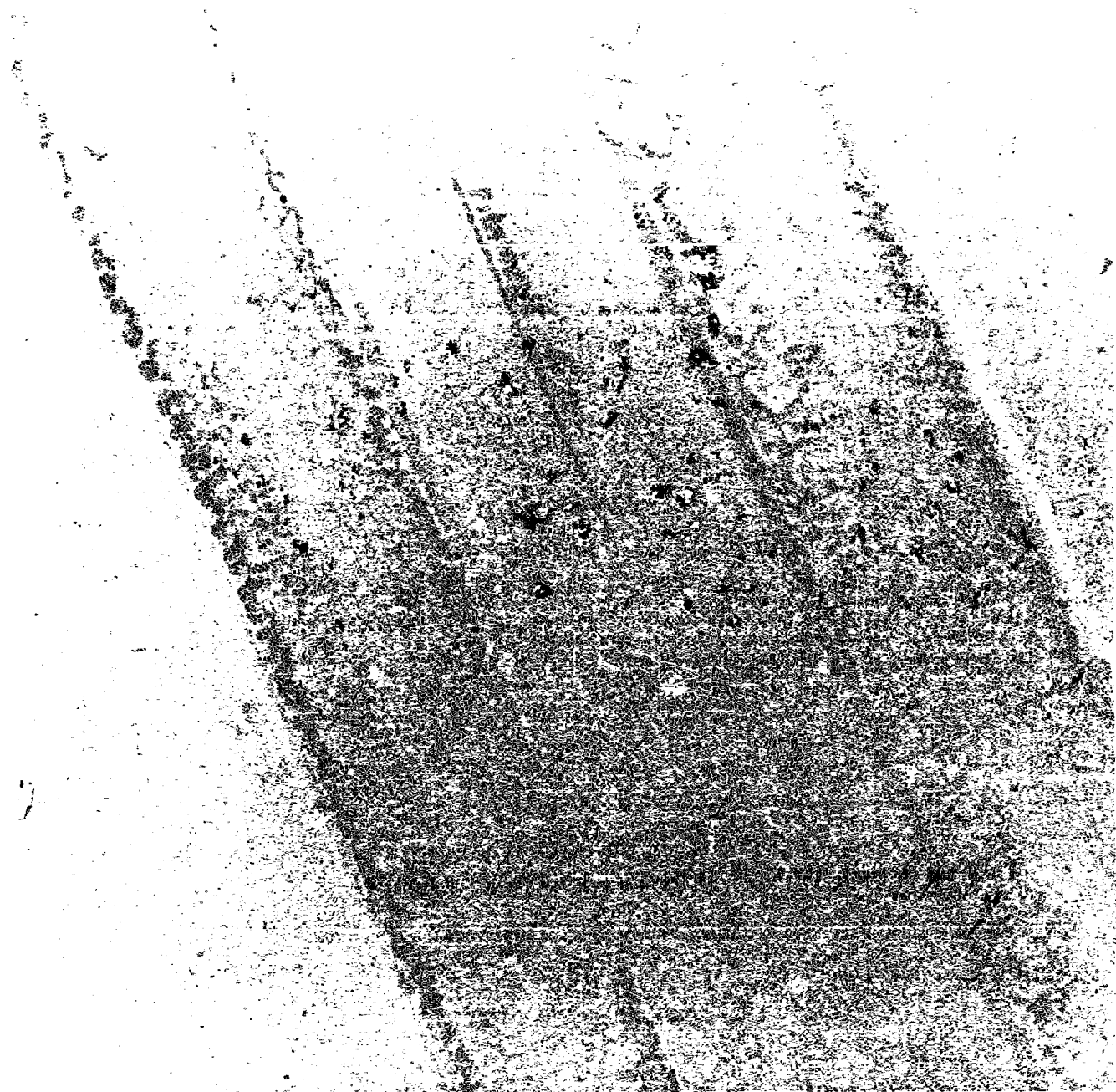


Figure 1

21,440 X

1 mm. = 0.0465 micron

1.6% A-1100 on Glass Cloth

Heavy Strips of A-1100 Finish Parallel to the Filament  
Axis at the Intersections of Filaments



Figure 2

80,960 X

1 mm.=0.0125 micron

A-1100 on Glass Cloth

Finish Retained after 4 Hours Extraction of 1.6% Loading with  
Hot Water; Less than 0.1% Loading Left

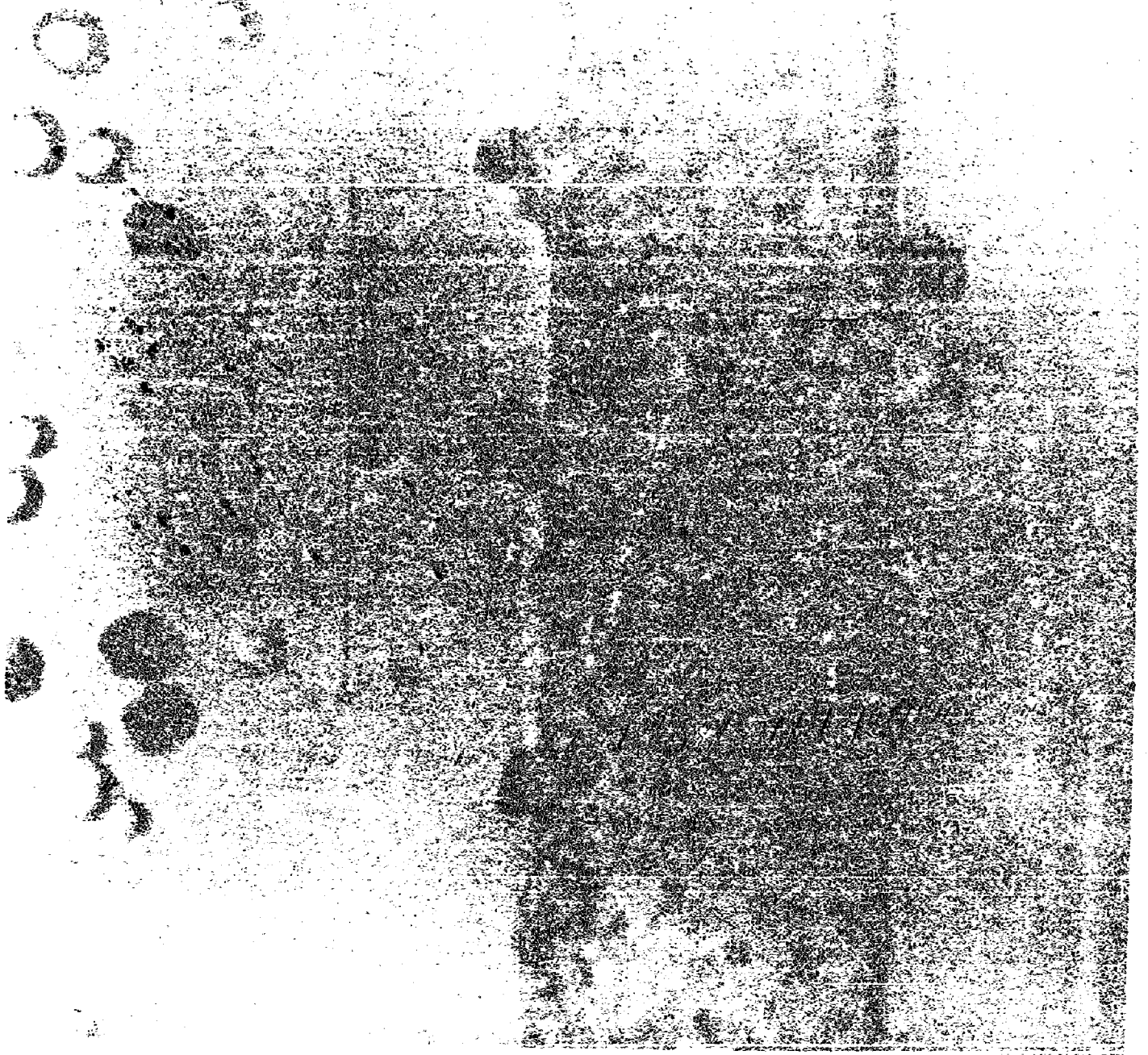


Figure 3

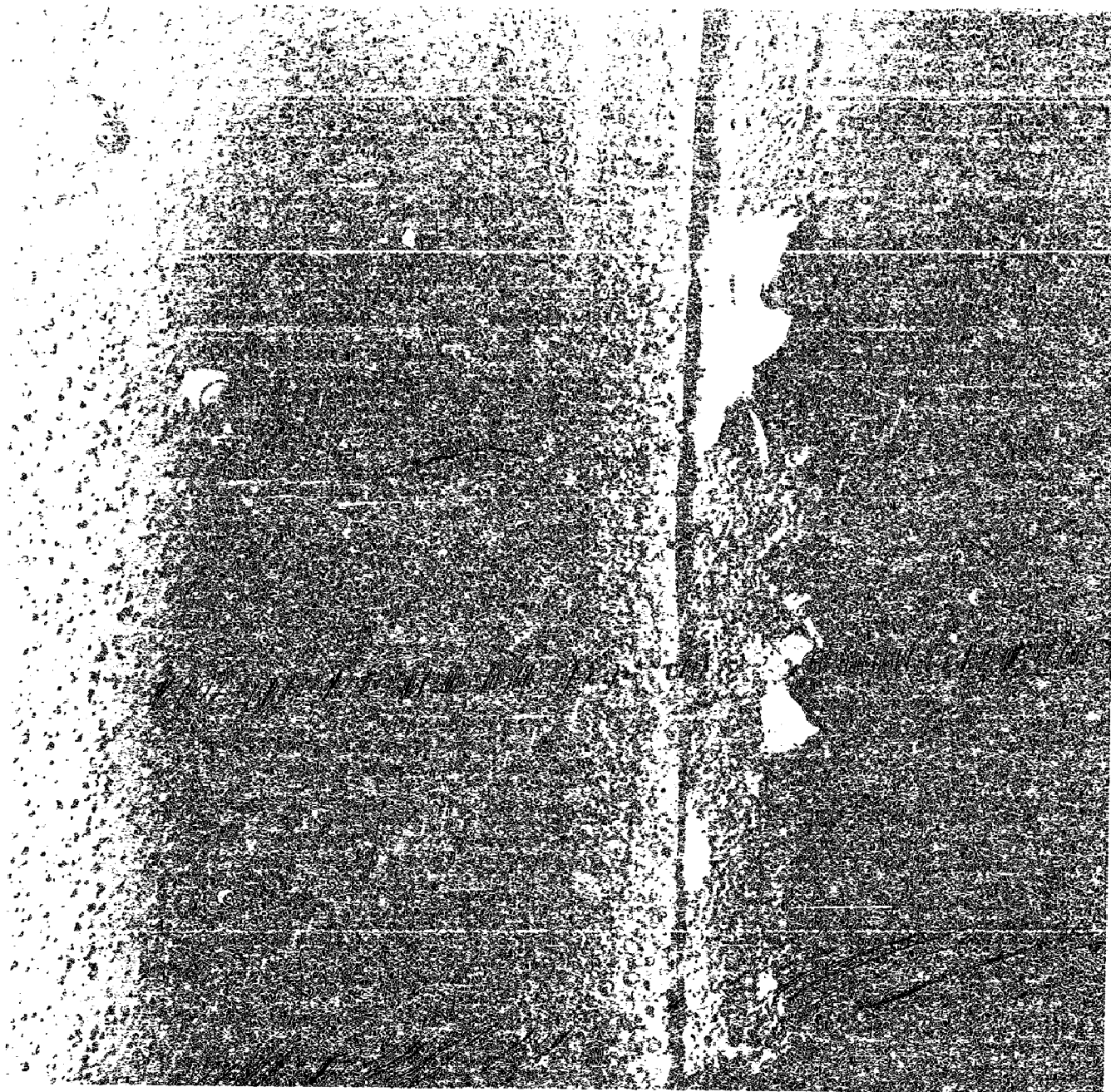
80,960 X

1 mm. = 0.0125 microns

0.1% A-1100 on Glass Cloth

Heavy Concentration in Inter-Filament Channels, even at this Low Loading. Compare with Figure 2 where loading was reduced from 1.6% to 0.1% by water extraction.





Inter-Filament Channel

Figure 4

9,240 X

1 mm. = 0.108 Micron

0.5% A-172 on Glass Cloth

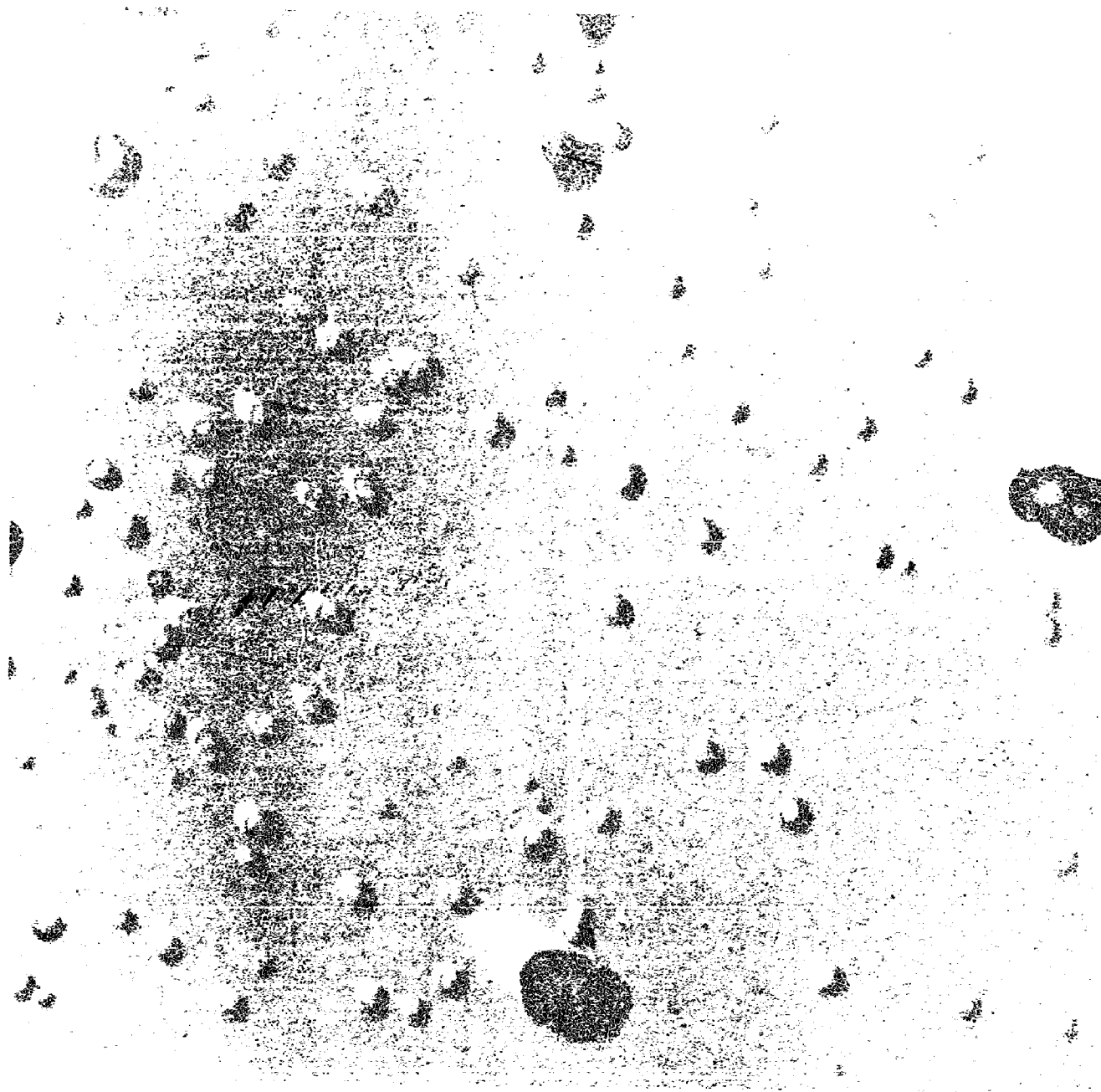


Figure 5

64,500 X

1 mm = 0.015 micron

A-172 on Glass Cloth

Loading: By Chemical Analysis	0.26%
Calculated from Picture	0.19%

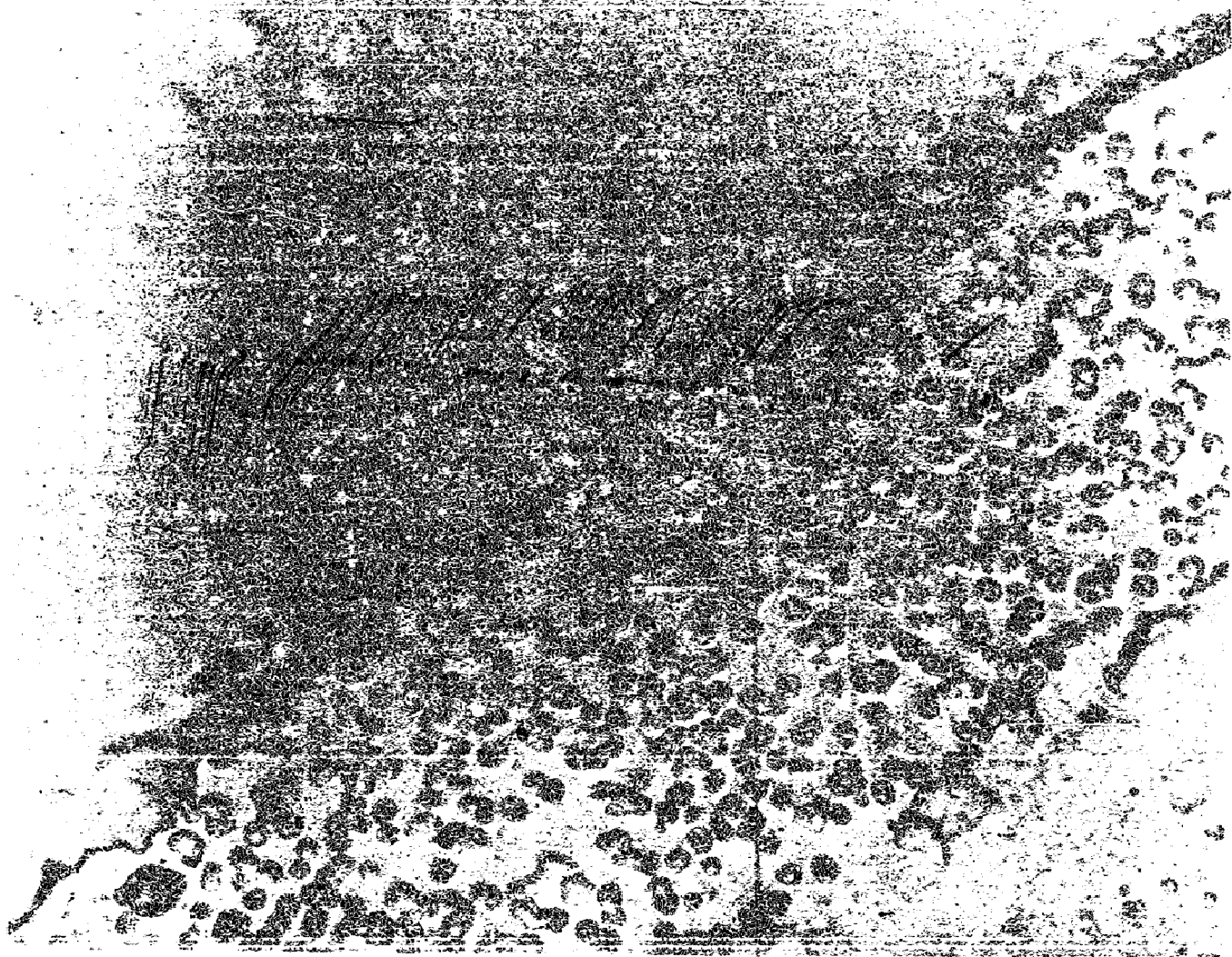


Figure 6

21,440 X

1 mm. = 0.0465 micron

A-172 on Glass Cloth

Average Loading by Chemical Analysis:	0.26%
Calculated Loading in Inter-Filament Channel:	2.43%

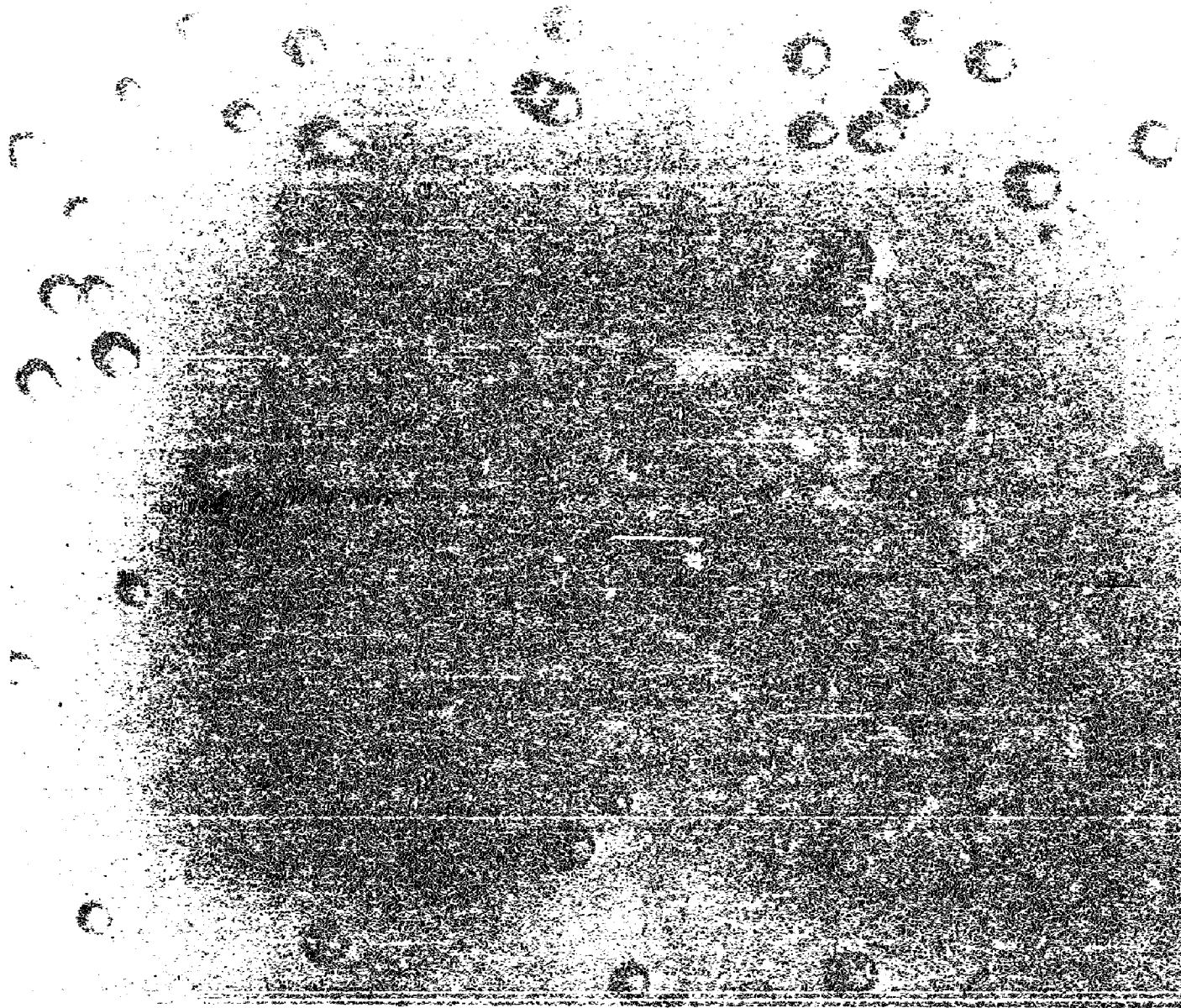


Figure 7

66,300 X

1 mm. = 0.015 micron

A-172 on Glass Cloth

Loading: By Chemical Analysis  
Calculated from Picture

0.03%  
0.05%



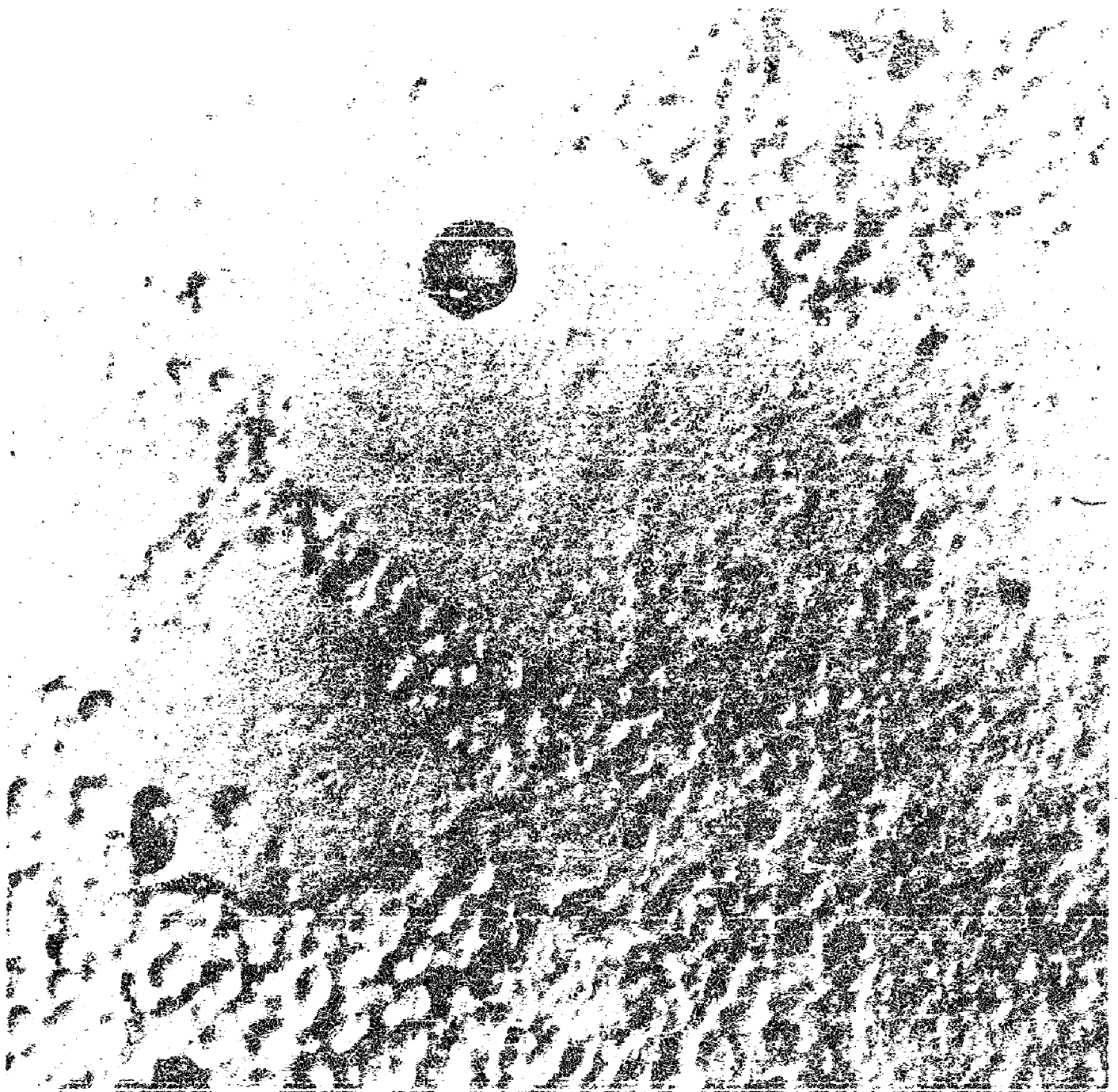


Figure 8

80,960 X

1 mm.  $\times$  0.0125 micron

Water Extracted A-172 Glass Cloth

Loading:	By Chemical Analysis	0.6%
	Calculated from Picture	0.3%

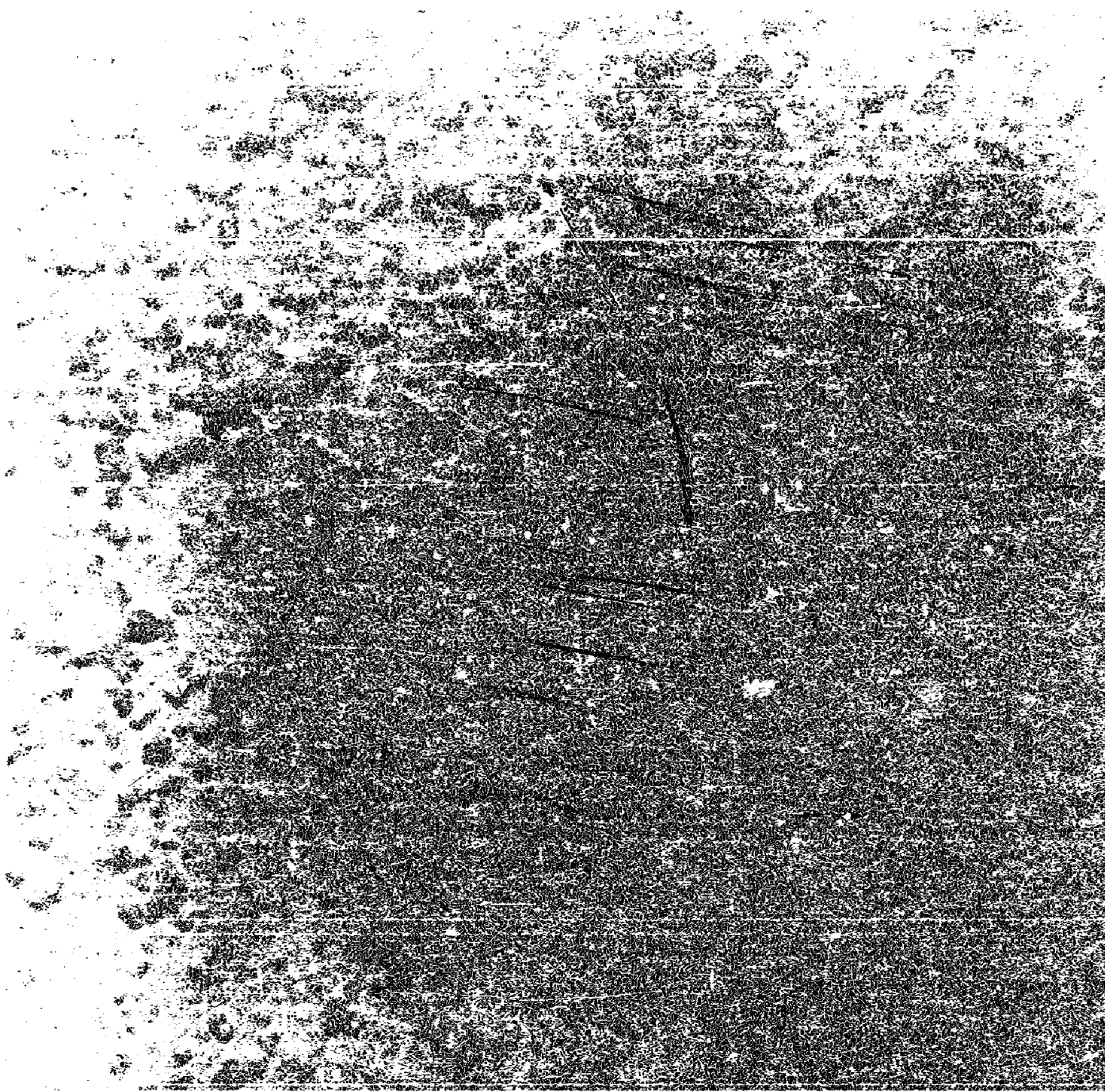


Figure 9

80,960 X

1 mm. = 0.0125 micron

Valen A on Glass Cloth

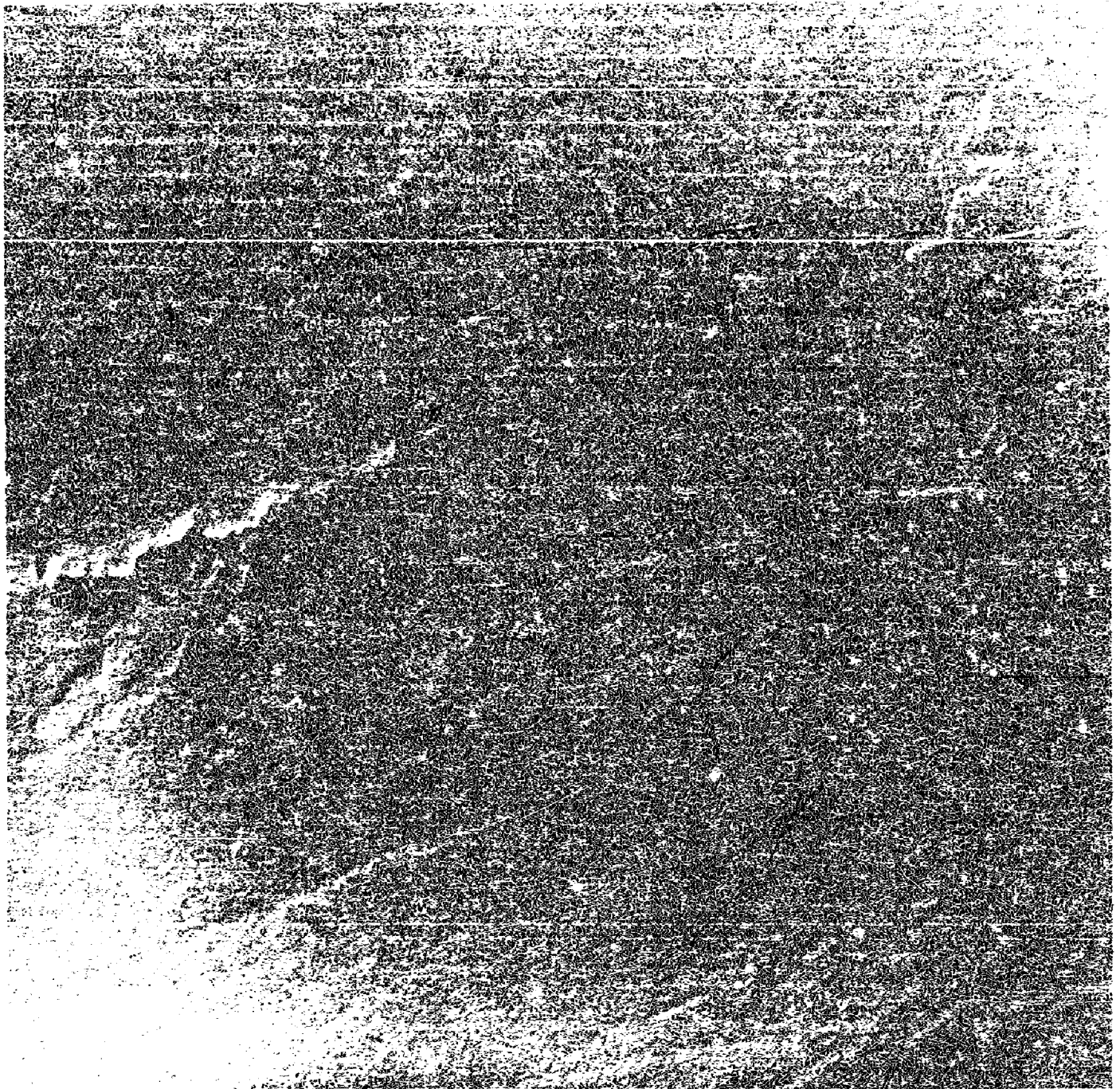


Figure 10

80,750 X

1 mm.  $\pm$  0.0125 micron

Black Glass Cloth:

Maximum Roughness of Unflashed Filaments

WADD TR 60-318 80



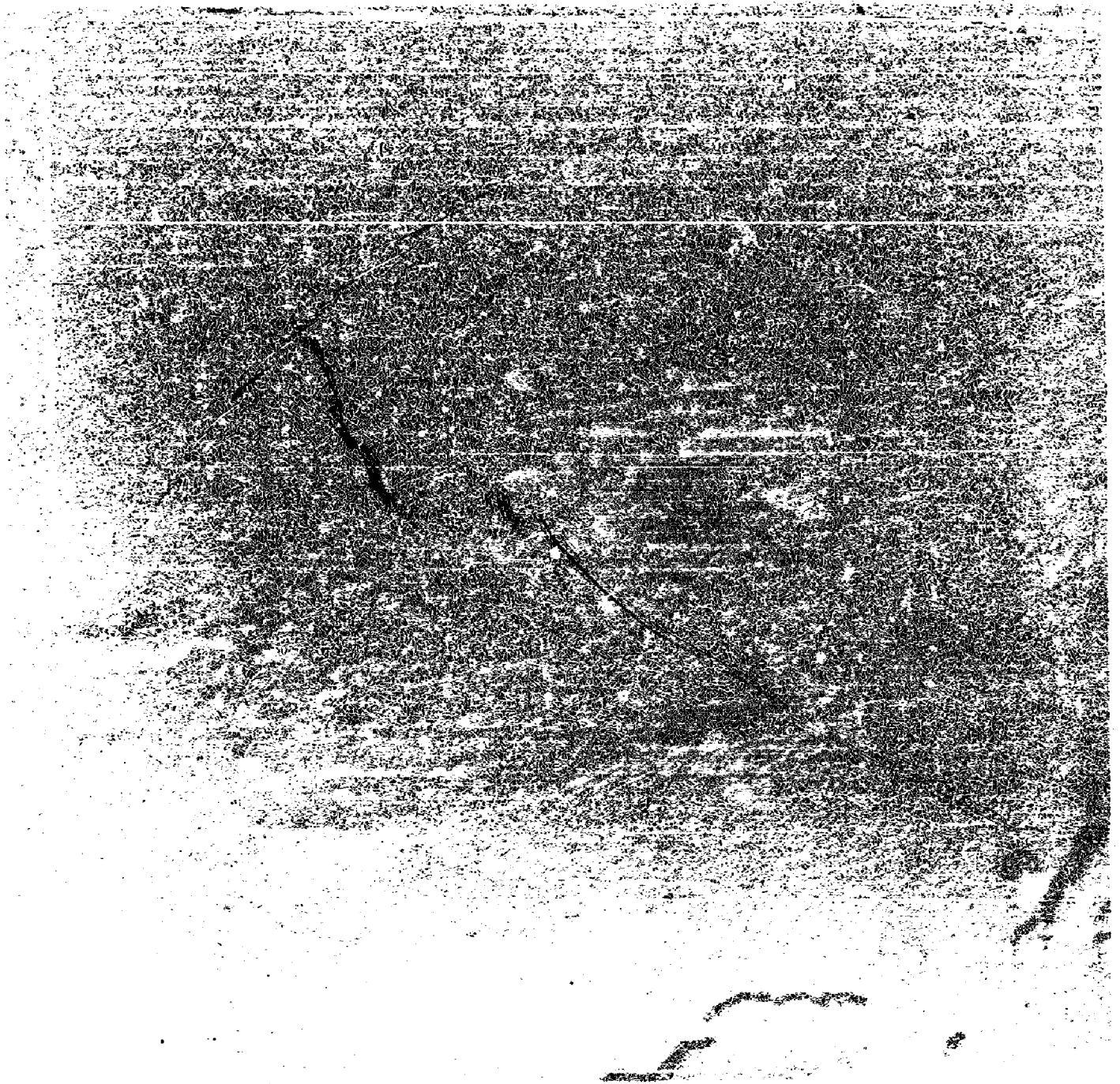


Figure 11

20,960 X

1 mm. = 0.0125 micron

Blank Glass Cloth

Surface Appearance of Average Unfinished Filaments



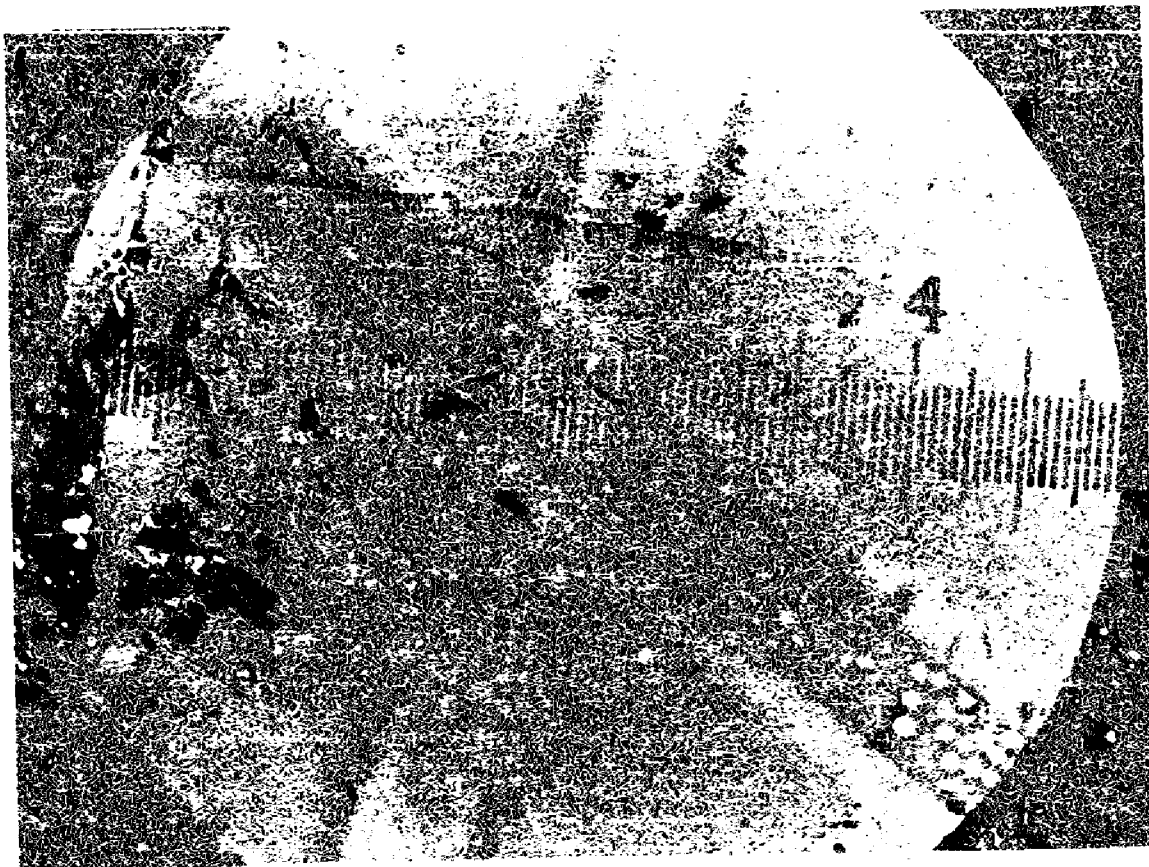


Figure 12

Light Microscope Photomicrograph  
of 1.6% A-172 on Glass Cloth

1 small division = 0.62 micron

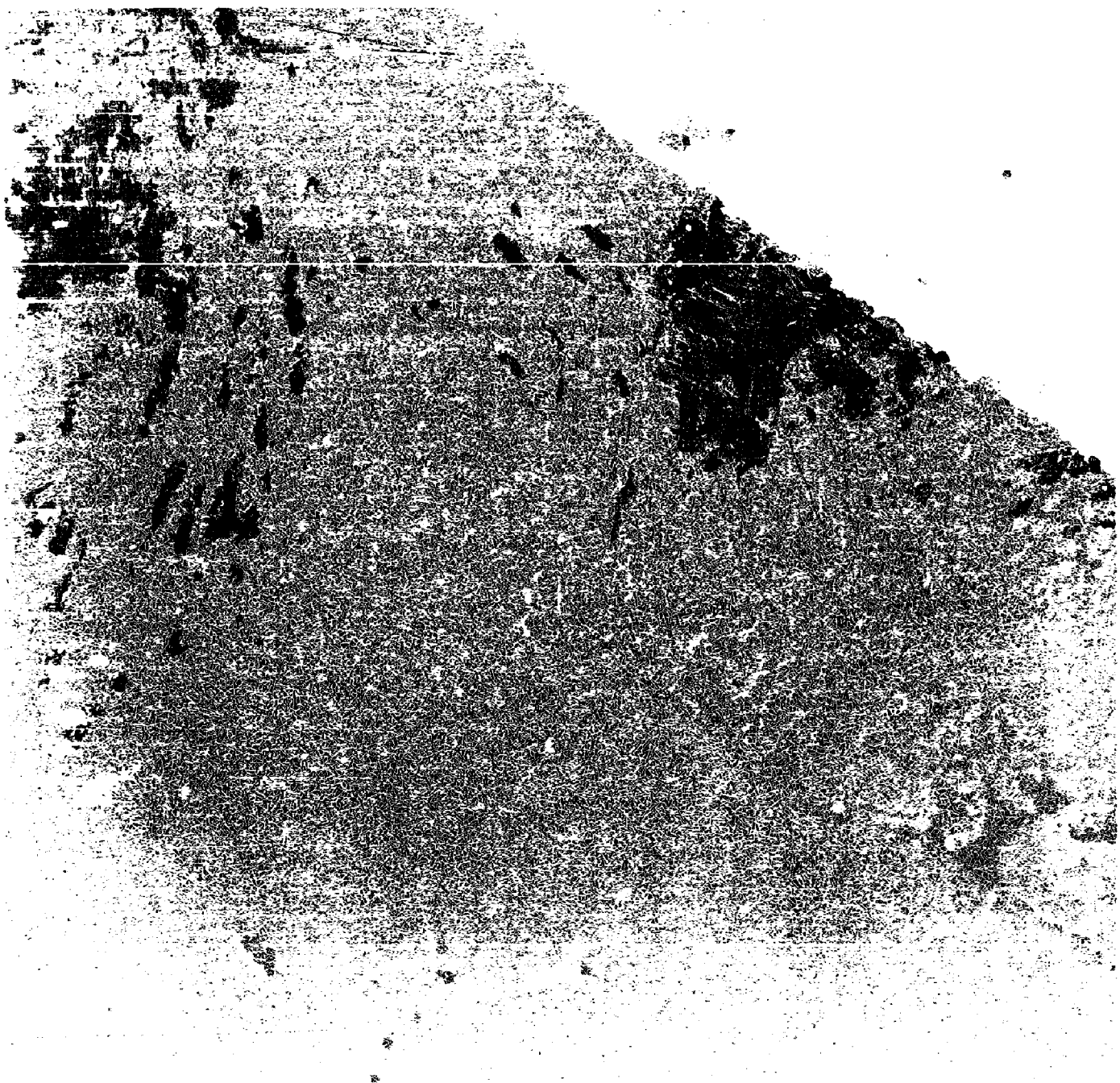


Figure 13

21,400 X

1 mm. = 0.047 micron

0.5% Valon A on Glass Cloth

Buildup at Inter-Filament Channel



Figure 14

80,900 X

1 mm = 0.0125 micron

0.5% Volcan A on Glass Cloth

Building of Inter-Filament Channel

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## METHYLENE BLUE COLOR TEST

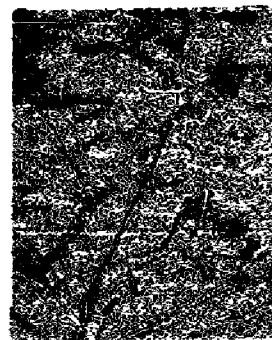
A-172



Volan

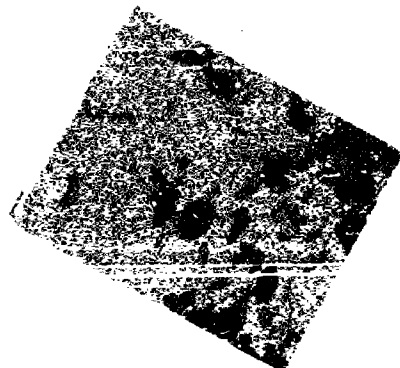
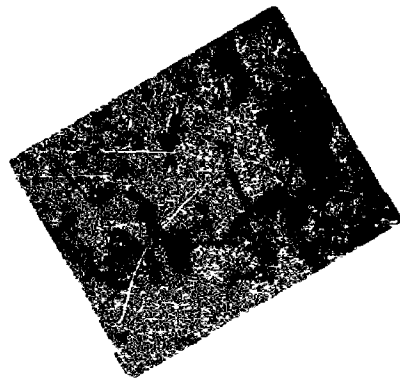
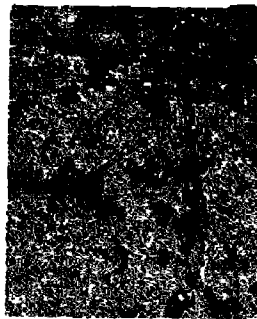


Blank



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**SIMULATED NITROPRUSSIDE - A-1100**  
**Colored Specimens**



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